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Publication No. US 2006/0211818 A1

Applicants: Hiroyuki Kurimura, et al

Application No.: 10/549,572

Publication No.: US 2006/0211818 A1

Filed: September 19, 2005

Publication Date: September 21, 2006

Title: BLOCK COPOLYMER MIXTURE CONTAINING
STAR-BRANCHED BLOCK COPOLYMER

Group Art Unit: 1711

Examiner: Mullis, Jeffrey C.

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IN A PUBLISHED APPLICATION UNDER 37 C.F.R. §1.99

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To Whom It May Concern:

Pursuant to 37 C.F.R. §1.99, a member of the public hereby submits the following patents or publications for consideration by the Office:

1. U.S. Patent No. 3,636,517, issued February 1, 1972;
2. U.S. Patent No. 4,091,053, issued May 23, 1978;
3. U.S. Patent No. 5,436,298, issued July 25, 1995;
4. U.S. Patent No. 5,705,569, issued January 6, 1998;
5. Kraus, G., et al, "Morphology and Dynamic Viscoelastic Behavior of Blends of Styrene-Butadiene Block Copolymers", Adv. Chem. Ser.; (1979), 176, 277-92
6. Hsieh, H.L., et al, "Kinetics of Alkylolithium Initiated Polymerizations", Rubber Chemistry and Technology (1970), 43(1), 22-73;

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Ricki J. Moss

11/22/2006 REF:ADU1 00000018 132725 10549572

01 FC:1806 160.00 DA

7. Knoll, K., et al, "Styrolus+ and Styroflex+ -- From Transparent High Impact Polystyrene to New Thermoplastic Elastomers. Syntheses, Applications and Blends with other Styrene based Polymers", Macromol. Symp. (1998), 132, 231-243;
8. U.S. Patent No. 4,086,298, issued April 25, 1978;
9. U.S. Patent No. 5,854,353, issued December 29, 1998; and
10. U.S. Patent No. 4,418,180, issued November 29, 1983.

The U.S. Patent and Trademark Office (PTO) is hereby authorized to charge the appropriate fee under 37 C.F.R. §1.17(p) for this submission.

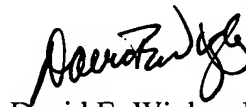
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In accordance with 37 C.F.R. §1.248(a)(4) and 37 C.F.R §1.248(b)(2), a copy of this submission was transmitted on November 20, 2006 via United States First Class Mail to the Applicant's attorney or agent at the following correspondence address listed on the published application:

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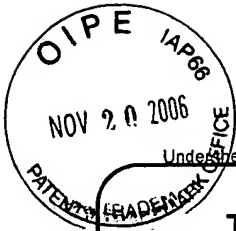
Respectfully submitted,



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11-21-06

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Application Number 10/549,572

Filing Date September 19, 2005

First Named Inventor Hiroyuki Kurimura

Art Unit 1711

Examiner Name Mullis, Jeffrey C.

Attorney Docket Number N/A

ENCLOSURES (Check all that apply)

<input checked="" type="checkbox"/> Fee Transmittal Form	<input type="checkbox"/> Drawing(s)	<input type="checkbox"/> After Allowance Communication to TC
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Firm Name	Merchant & Gould, LLC		
Signature			
Printed name	David E. Wigley, Ph.D.		
Date	November 20, 2006	Reg. No.	52,362

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FEE TRANSMITTAL For FY 2006

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$) 180.00

Complete if Known

Application Number 10/549,572
Filing Date September 19, 2005
First Named Inventor Kiroyuki Kurimura
Examiner Name Mullis, Jeffrey C.
Art Unit 1711
Attorney Docket No. N/A

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METHOD OF PAYMENT (check all that apply)

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FEE CALCULATION

1. BASIC FILING, SEARCH, AND EXAMINATION FEES

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	-
Design	200	100	100	50	130	65	-
Plant	200	100	300	150	160	80	-
Reissue	300	150	500	250	600	300	-
Provisional	200	100	0	0	0	0	-

2. EXCESS CLAIM FEES

Fee Description

	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180

Total Claims Extra Claims Fee (\$) Fee Paid (\$)

- 20 or HP = x =

HP = highest number of total claims paid for, if greater than 20.

Indep. Claims Extra Claims Fee (\$) Fee Paid (\$)

- 3 or HP = x =

HP = highest number of independent claims paid for, if greater than 3.

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets Extra Sheets Number of each additional 50 or fraction thereof Fee (\$) Fee Paid (\$)

- 100 = / 50 = (round up to a whole number) x =

4. OTHER FEE(S)

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Other (e.g., late filing surcharge): Fee for Third-Party Submission of Prior Art 180.00

SUBMITTED BY

Signature David E. Wigley Registration No. (Attorney/Agent) 52,362 Telephone 404-954-5056
Name (Print/Type) David E. Wigley, P.D. Date November 20, 2006

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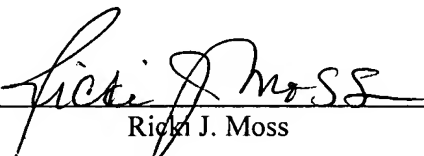
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Rick J. Moss



Feb. 1, 1972

A. G. KITCHEN ETAL

3,639,517

RESINOUS BRANCHED BLOCK COPOLYMERS

Filed Sept. 22, 1969

3 Sheets-Sheet 1

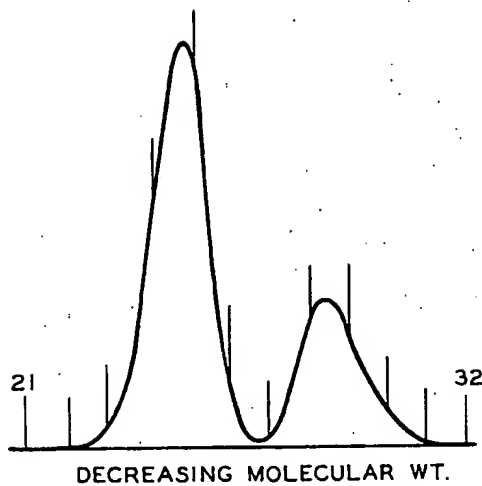


FIG. 1b

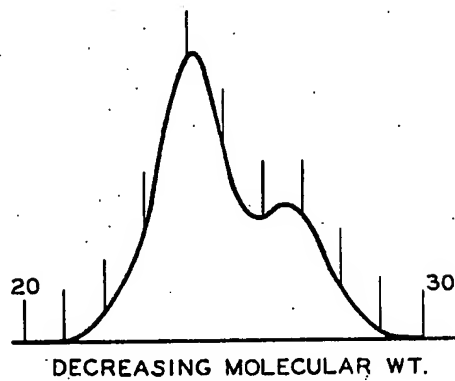


FIG. 1d

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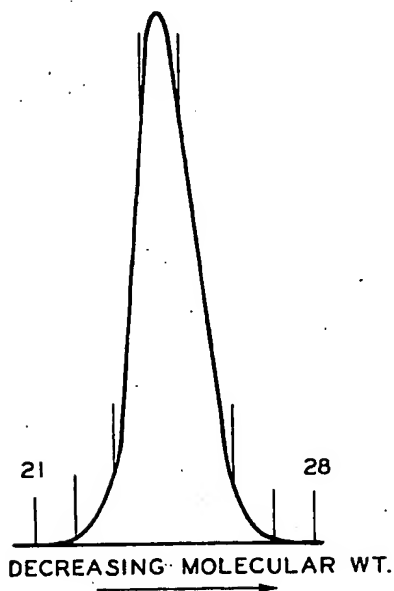


FIG. 1a

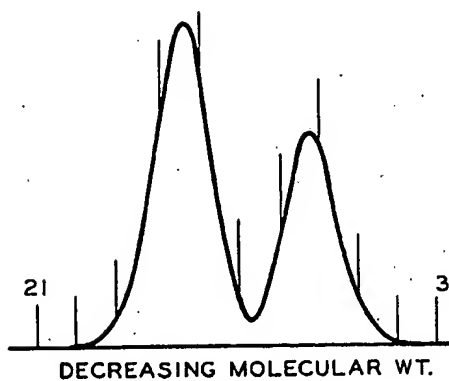


FIG. 1c

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F. J. SZALLA

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Young and Quigg

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Feb. 1, 1972

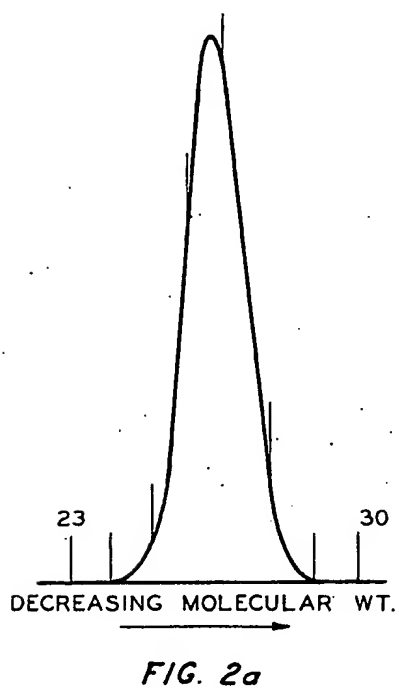
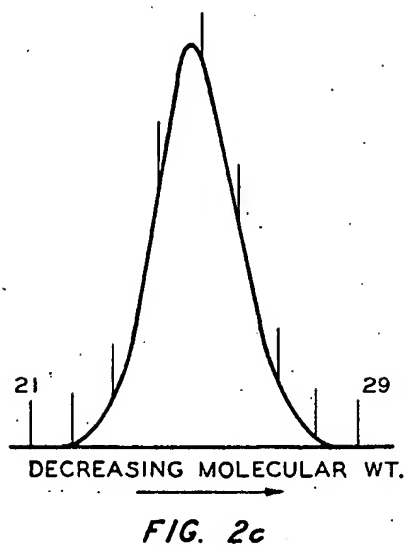
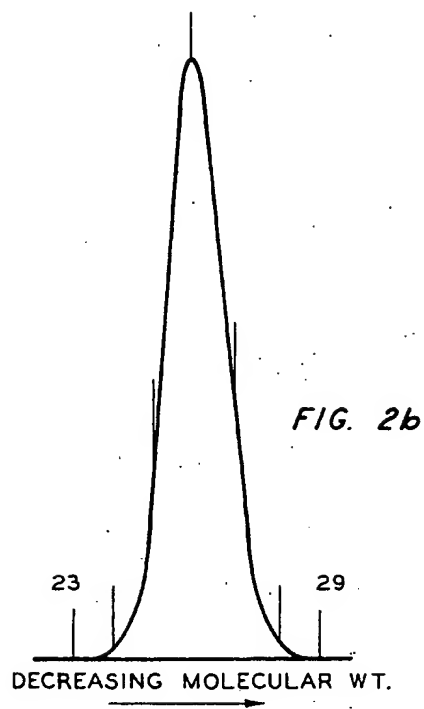
A. G. KITCHEN ETAL

3,639,517

RESINOUS BRANCHED BLOCK COPOLYMERS

Filed Sept. 22, 1969

3 Sheets-Sheet 2



INVENTORS
A. G. KITCHEN
F. J. SZALLA

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Feb. 1, 1972

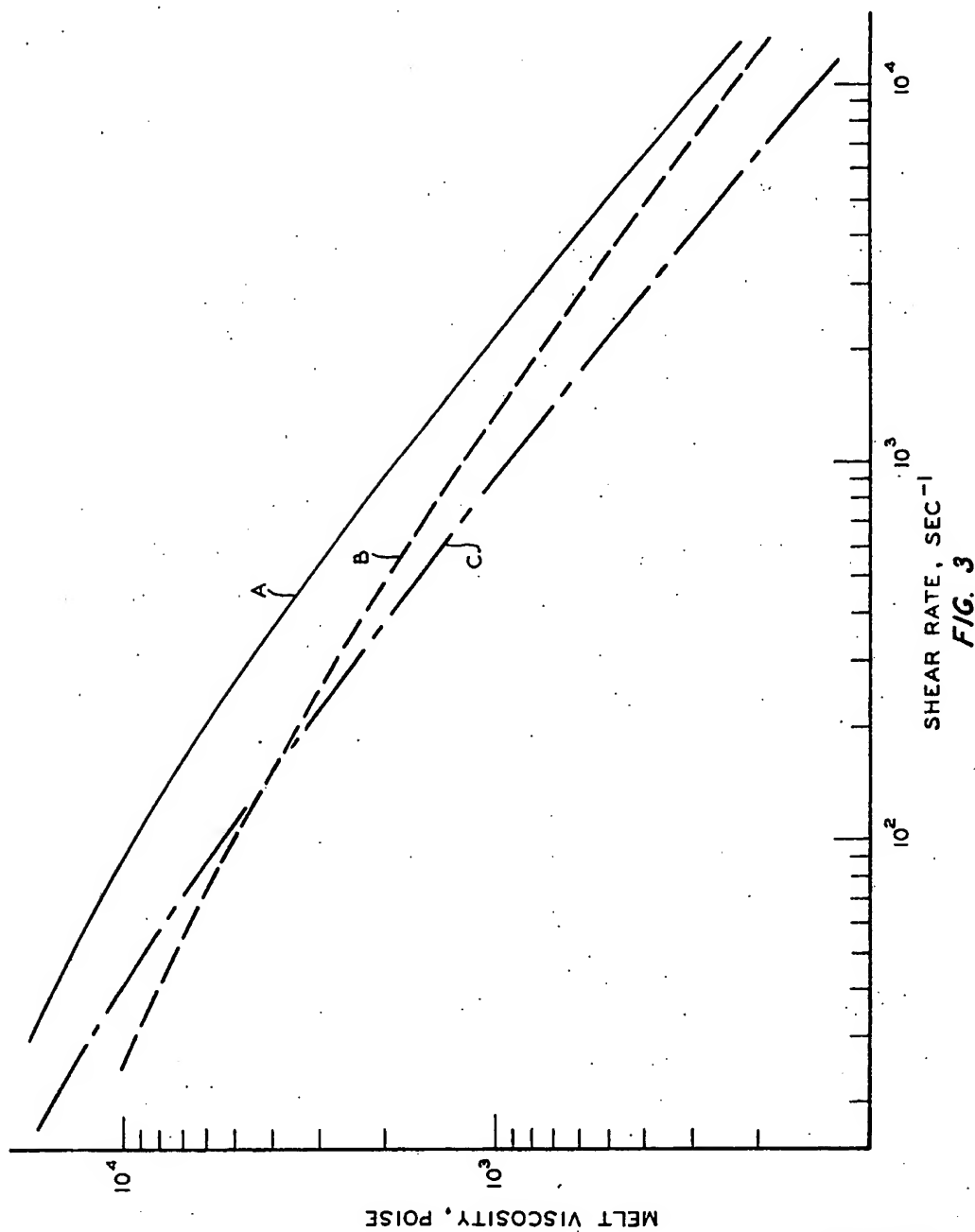
A. G. KITCHEN ETAL

3,639,517

RESINOUS BRANCHED BLOCK COPOLYMERS

Filed Sept. 22, 1969

3 Sheets-Sheet 3



INVENTORS
A. G. KITCHEN
F. J. SZALLA

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1

3,639,517

RESINOUS BRANCHED BLOCK COPOLYMERS
Alonzo G. Kitchen and Frank J. Szalla, Bartlesville,
Okla., assignors to Phillips Petroleum Company
Filed Sept. 22, 1969, Ser. No. 859,861

Int. Cl. C08f 19/08

U.S. Cl. 260—879

12 Claims

ABSTRACT OF THE DISCLOSURE

Monovinyl-substituted aromatic hydrocarbons and conjugated dienes are sequentially polymerized with multiple additions of initiator and monovinyl-substituted aromatic monomer and subsequently treated with a polyfunctional treating agent to form resinous branched block copolymers which are polymodal in regard to molecular weight distribution.

This invention relates to novel polymodal resinous thermoplastic branched block copolymers and to articles manufactured therefrom.

In another aspect this invention relates to a novel polymerization process for the production of polymodal resinous branched block copolymers which can be molded into transparent articles.

There has developed in the polymer field, and especially in the packaging and related industries, a need for thermoplastic polymers that can be formed into transparent articles having high impact strength and which are suitable for use with conventional injection and blow molding equipment and also suitable for use in other methods of forming plastics into containers, tubes, films, fibers, and the like. Polystyrene, high impact polystyrene, branched block copolymers, and the like, have been developed with various degrees of satisfaction to meet these criteria. A resinous polymer that can be formed into articles that possess a combination of good stiffness and impact strength, as well as being transparent, is definitely in demand in the polymer field. Polymer articles that have satisfactory clarity, such as those made from polystyrene polymers, are lacking in impact strength. Articles formed from blends of polymers, such as high impact polystyrene, often possess the satisfactory impact strength but lack sufficient clarity or other requisite properties. Blends of polystyrene with various compounds such as butadiene-styrene copolymers have been developed but as the impact strength of these plastic articles is increased there is also an increase in the opaqueness of the article and therefore they too have limited application. Polymers that can be employed to form articles possessing good clarity and strength often pose difficulties when processing them in conventional equipment. There is therefore a recognized need for suitable polymers in the packaging and related industries, especially in the food packaging industry where large varieties of products are employed. It is essential in food packaging that the articles employed to contain these products do not fail and allow leakage, contamination, etc., of the product. A particularly difficult problem is encountered when the plastic containers are employed for food products having oily bases such as butter, lard, margarine, cooking oil, and the like. The environmental

2

stresses created by these oily bases often result in failure of the container.

Summarily, a polymer suitable for use in forming transparent articles possessing high impact strength and high environmental stress resistance while possessing good processability in conventional equipment is particularly needed.

A novel resinous branched block copolymer has now been discovered that surprisingly fulfills all of these requirements and thus combines the attributes of strength, clarity, processability, and environmental durability into a single polymer.

The polymers of this invention can be broadly described as branched block copolymers and are an improvement on the prior art branched block copolymers, such as described in U.S. Pat. 3,281,383, issued to Zelinski et al. Oct. 25, 1966. Zelinski et al. have therein conveniently referred to their branched polymers as radial polymers because they have relatively long polymer branches radiating from a nucleus formed from a polyfunctional treating or coupling compound. These radial polymers possess many excellent properties and are particularly described therein as having little if any tendency to undergo cold flow, and yet have better processing properties than other polymers of comparable Mooney values prepared by prior art methods. The polymers prepared according to the preferred process of the instant invention can also be broadly referred to as radial polymers although they are distinguishable over the prior art radial polymers and possess even more outstanding properties.

The polymers prepared according to this invention are polymodal, resinous, branched block copolymers and contain from about 70 to 95 weight percent of polymerized monovinyl-substituted aromatic hydrocarbon monomer based on the weight of the total monomers employed. The polymers of this invention when formed into articles not only exhibit surprising and outstanding properties such as impact strength and high environmental stress cracking resistance but are transparent as well. The polymers also exhibit remarkable processability and can be employed in conventional processing equipment with ease.

The polymers of this invention are prepared by a novel polymerization process employing the sequential polymerization of monovinyl-substituted aromatic hydrocarbon and conjugated dienes. The non-elastomeric blocks or segments are first formed by multiple additions of monovinyl-substituted aromatic hydrocarbon monomer and organolithium initiator. Subsequently, the conjugated diene is added and polymerized to form an elastomeric polymer block followed by the addition of a polyfunctional treating agent. The multiple addition or charging of the monovinyl-substituted aromatic hydrocarbon monomer and the organolithium initiator must be made at particularly described concentrations.

It is thus an object of this invention to provide a novel branched block copolymer. It is an object of this invention to provide a process for producing polymodal resinous block copolymers which can be formed into transparent articles. It is an object of this invention to provide a polymer that can be easily processed and formed into articles that exhibit high impact strength and environmental stress cracking resistance. It is a further object

of this invention to fulfill a need in the packaging industry by providing a polymer suitable for making articles possessing the particularly desired properties of strength, clarity and stability. Further objects and advantages of this invention will become apparent to those skilled in the art from the following description and discussion herein set forth.

FIGS. 1(a) through 1(d) and 2(a) through 2(c) represent gel permeation chromatograph curves of polymer obtained in the preparation of polymodal and regular radial polymers respectively. FIG. 3 is a log-log plot of melt viscosity versus shear rate in reciprocal seconds of various polymodal and regular radial polymers.

According to our invention a polymodal branched block copolymer is produced that possesses excellent processability. Articles prepared from said polymers possess excellent transparency, outstanding strength characteristics as well as excellent environmental stress cracking resistance.

Specifically, in our polymerization process, non-elastomeric (resinous) blocks of polymer must be first formed. The resinous portion of the block copolymer is formed by charging a substantial portion of the total amount of monovinyl-substituted aromatic hydrocarbon monomer employed to a polymerization vessel and contacting said monomer with a relatively small amount of organolithium initiator and maintaining polymerization conditions for a period of time sufficient to convert essentially all of the monomer and the initiator to relatively long non-elastomeric chains of living polymer having active terminal lithium atoms.

The remainder of the total monovinyl-substituted aromatic hydrocarbon monomer employed is then charged in one or more increments, to said polymerization vessel containing the polymerization reaction product of the first charge such that each incremental charge of monomer is accompanied by a corresponding incremental charge of initiator so that a relatively large amount of initiator is employed per amount of monomer. The polymerization conditions are maintained and after each incremental charge of monomer and initiator a sufficient time is allowed to convert essentially all of the newly added monomer and initiator to non-elastomeric chains of living polymer.

After the non-elastomer polymer fraction has been prepared, the chains of non-elastomeric living polymer are contacted with conjugated diene monomer which is charged to the polymerization vessel and the reaction mixture is allowed to polymerize again to essential completion to form chains of living copolymer containing both elastomeric and non-elastomeric blocks.

The polyfunctional treating agent is then added to the polymerization mixture under reaction conditions sufficient to form branched copolymers containing both the elastomeric and non-elastomeric blocks. Thus, the polyfunctional treating agent is added to the polymerization mixture after the polymerization has been essentially completed but prior to deactivation of the polymerization initiator.

The polymer can be recovered after the polyfunctional treating agent has formed the branched block copolymers. Recovery of the polymers can be by conventional methods used for recovering polymer from organometal polymerization mixtures such as by treatment with materials containing active hydrogen such as alcohols, aqueous acids, and the like.

As hereinbefore stated, the non-elastomeric polymer fraction is first formed by the multiple addition of both the monomeric material and polymerization initiator. At least two additions of the monovinyl-substituted aromatic hydrocarbon and the polymerization initiator are required.

In the first addition step the monovinyl-substituted aromatic hydrocarbon is added in an amount to provide from about 40-90 weight percent preferably at least 60 weight percent of the total monovinyl-substituted aromatic

hydrocarbon employed in the total copolymer composition. An organolithium initiator is employed with said first addition step in an amount to provide from about .01 to 0.2 part by weight per 100 parts by weight of monomer employed in said first addition. This first charge of monovinyl-substituted aromatic hydrocarbon, representing about 40-90 weight percent of the total monovinyl-substituted aromatic hydrocarbon monomer employed in preparing the block copolymer, is then allowed to polymerize to essential completion.

The remaining monovinyl-substituted aromatic hydrocarbon monomer, i.e., from about 10 to 60, preferably less than 40, weight percent of the total monovinyl-substituted aromatic hydrocarbon employed, is charged, in one or more increments, to this reaction mixture. For each incremental charge of monomer there is another charge of organolithium polymerization initiator. The polymerization initiator is preferably charged to said reaction mixture prior to charging said remaining monovinyl-substituted aromatic hydrocarbon monomer. From about 0.1 to about 1.5 parts of organolithium polymerization initiator per 100 parts of monomer employed in each incremental charge of the monovinyl-substituted aromatic hydrocarbon monomer is also added. After each incremental charge of monomer and initiator a sufficient time is then allowed to polymerize the newly added monomer to essential completion. Although it is preferred to employ only two charges of monovinyl-substituted aromatic hydrocarbon monomer, more than two additions can be made if desired by dividing the second described monomer charge, i.e., representing 10-60 weight percent, into as many increments as wanted.

At the completion of the multiple additions and subsequent polymerizations of the monovinyl-substituted aromatic hydrocarbon, the conjugated diene monomer, representing from about 30-5 weight percent of the total monomeric material employed in the polymer preparation, is charged to the reaction mixture and is allowed to form a block copolymer with the previously polymerized monovinyl-substituted aromatic hydrocarbon monomer. No additional initiator is added with the diene charge. The conjugated diene is converted to the copolymer by contact with the reactive terminal lithium atoms of the previously prepared living non-elastomeric polymer.

Summarily, the first addition of initiator accompanies the first monovinyl-substituted aromatic monomer addition and is added in an amount to provide from about .01 to 0.2, preferably 0.03 to 0.10 part by weight of initiator per 100 parts by weight of monomer. The second addition of initiator is charged in an amount to provide from about 0.1 to 1.5, preferably 0.3 to 1.5 parts by weight of initiator per 100 parts by weight of the monomer then charged. In order to obtain the improved results of the present invention, the proportion of initiator to monomer in all monomer-initiator additions beyond the first should be substantially greater than that of the first addition. Thus, the amount of initiator per 100 parts of monomer in the later additions should exceed that of the first by at least about 0.1 and preferably by at least about 0.2 part initiator per 100 parts monomers by weight.

It should be understood that various impurities or catalyst poisons may be present in the monomers, solvents, and reaction apparatus employed and adjustments may be necessary in the initiator level to provide the requisite amounts of active initiator levels over and above the amounts destroyed by such catalyst poisons. The determination of the "poison level" of a catalytic system is a conventional operation and within the skill of the art.

The monovinyl-substituted aromatic hydrocarbon monomers, or mixtures thereof, that are employed according to this invention contain from about 8-18 carbon atoms per molecule. Examples of suitable compounds include: styrene, 3-methylstyrene, 4-n-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzyl-

styrene, 4-p-tolylstyrene, 4-(4-phenyl-n-butyl)styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and the like. The monovinyl-substituted aromatic hydrocarbon can contain alkyl, cycloalkyl, and aryl substituents, and combinations thereof such as alkylaryl in which the total number of carbon atoms in the combined substituents is generally not greater than 12. Styrene is presently preferred because of its availability and effectiveness.

Conjugated dienes, and mixtures thereof, that can be employed as monomers according to this invention generally contain from about 4-12 carbon atoms per molecule and those containing from about 4-8 carbon atoms are preferred. Exemplary of suitable compounds are: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, phenyl-1,3-butadiene, and the like. Butadiene-1,3 is particularly effective and presently preferred.

The polymerization initiators employed according to this invention are well known and can be broadly depicted as organolithium initiators. Those preferred are hydrocarbyl monolithium compounds and can be represented by the formula RLi wherein R is a hydrocarbon radical selected from aliphatic, cycloaliphatic, or aromatic radicals containing from about 1 to 20 carbon atoms per molecule. Exemplary initiators suitable for use according to this invention include: n-butyllithium, sec-butyllithium, methylolithium, phenyllithium, naphthyllithium, p-tolylolithium, cyclohexyllithium, eicosyllithium, and the like. Because it is particularly effective, n-butyllithium is presently preferred.

As previously outlined, at the conclusion of the polymerization of the conjugated diene a polyfunctional treating agent containing at least two functional groups capable of reacting with the terminal lithium atoms on the preformed polymer is employed to form a branched polymer. It is preferred, however, to employ polyfunctional treating agents having at least three functional groups.

The polymer formed following reaction with the polyfunctional treating agent having at least three functional groups can be broadly characterized as a radial polymer. If a difunctional treating agent is employed to form the branched block copolymers of this invention, it must itself be a monomeric material capable of addition to itself under polymerization conditions.

Some polyfunctional treating agents that can be employed according to this invention in the preparation of the branched block copolymers are the polyepoxides such as epoxidized linseed oil and 1,2,5,6,9,10-triepoxydecane, polyimines such as tri(1-aziridinyl)phosphine oxide, polyisocyanates such as benzene-1,2,4-trisocyanate, polyaldehydes such as 1,4,7-naphthalene tricarboxyaldehyde, polyhalides such as silicon tetrachloride or polyketones such as 1,4,9,10-anthracenetetrone. The aforementioned treating agents are described in U.S. Patent 3,281,383, issued to Zelinski et al. Oct. 25, 1966, and are hereby incorporated by reference thereto. Tin compounds disclosed in U.S. Patent 3,393,182, issued to Trepka July 16, 1968, are also suitable. Exemplary compounds are tetraallyltin, stannic fluoride, and the like. The polyvinyl aromatic compounds as disclosed in U.S. Patent 3,280,084, issued to Zelinski et al. Oct. 18, 1966, such as divinylbenzene are suitable difunctional treating agents.

The particular polyfunctional treating agent employed in this invention is not critical so long as said agent is capable of forming branched polymer by reacting with active terminal lithium atoms of a living polymer provided that said agent does not substantially impair the desired properties of the final polymer. The number of functional groups per molecule of the polyfunctional treating agent employed in the preparation of the branched block copolymer is preferably at least 3. The treating agents such as those disclosed in U.S. Patent 3,280,084, i.e., polyvinyl aromatic compounds which are themselves monomeric materials such as divinylbenzene are suitable for use in this invention in that they provide a branched

block copolymer but not necessarily a typical radial polymer.

The polyfunctional treating agent is employed in an amount sufficient to provide from about 0.05 to 2, preferably 0.5 to 1.5, equivalents of said agent per gram atom of lithium employed in the initiator. One functional group of said polyfunctional treating agent, i.e. one equivalent is the optimum amount to be employed per gram atom of lithium. The polyfunctional treating agent is added to the polymerization mixture after the polymerization has been completed and prior to the deactivation of the initiator.

In order to prepare a polymer possessing the hereinbefore described attributes the polymerization is conducted at any temperature suitable for polymerization up to about 250° F., preferably below about 230° F.

The polymerization reaction can be conducted under autogenous pressure. It is usually desirable to operate at pressures sufficient to maintain the monomeric material substantially in the liquid phase.

Polymerization can be conducted in the presence or absence of diluent. Inert hydrocarbon diluents selected from aromatics, paraffins, or cycloparaffins, and mixtures thereof, containing from about 4 to 10 carbon atoms per molecule can be suitably employed. The diluent or diluent mixture is one which is liquid under conditions of the polymerization process and exemplary diluents are isobutane, n-pentane, cyclohexane, benzene, toluene, xylene, naphthalene, and the like. As in all such catalytic reactions, the polymerization are conducted in the substantial absence of air or moisture, preferably in an inert atmosphere.

Small amounts of an ether compound, such as tetrahydrofuran, can also be employed in the polymerization reaction. Amounts of tetrahydrofuran to provide from about .005 to 5 weight percent of tetrahydrofuran based on the total monomer charge, preferably .05 to .1 weight percent, are considered suitable. The tetrahydrofuran appears to reduce the induction period of some of the initiators, such as n-butyllithium, and its presence appears active in improving the clarity of final polymer articles.

The branched block copolymers formed when the polyfunctional treating agent contains at least three functional groups can be broadly depicted as an $(A-B)_xY$ type polymer, wherein A represents the non-elastomeric polymer blocks or segments and B represents the elastomeric polymer segments. Y is an atom or group of atoms derived from the polyfunctional treating agent used in the formation of the radial polymers and x represents the number of functional groups of said polyfunctional treating agent and is an integer of at least 3.

The radial block copolymers produced according to this invention using a polyfunctional treating agent having at least three functional groups can thus be characterized as having at least three polymer branches with each branch of the radial block copolymer comprising terminal non-elastomeric segments. The branches of the radial block copolymer thus contain terminal non-elastomeric segments and an elastomeric polymer segment joined thereto.

Regardless of the polymer configuration, the terminal non-elastomeric segments of the polymodal branched block copolymer comprise from about 70 to 95, preferably 75 to 85 weight percent of the total weight of the block copolymer with the elastomeric segments comprising about 30 to 5, preferably about 25 to 15 weight percent of the total weight of the block copolymer based upon the total weight of all the monomers charged.

Subject to the above limitations, the terminal non-elastomeric segments can contain small quantities of polymerized conjugated diene monomer and the elastomeric segment can contain small quantities of polymerized monovinyl-substituted aromatic hydrocarbon such as in a random copolymer.

It is important that each of the polymer segments retain their relative non-elastomeric and elastomeric properties but as long as these small amounts of different monomeric

material do not substantially affect their relative properties they can be employed. Generally, the non-elastomeric segments should not contain more than 30 weight percent polymerized conjugated diene nor the elastomeric segment more than 30 weight percent polymerized monovinyl-substituted aromatic hydrocarbon.

According to our invention, however, it is preferred that each of the non-elastomeric segments and elastomeric segments be homopolymers of monovinyl-substituted aromatic hydrocarbon and conjugated diene, respectively.

The new polymers produced according to this invention are further characterized as polymodal branched block copolymers. The term polymodal refers to the plurality of modes or peaks in the gel permeation chromatograph curve of our polymers, i.e., the molecular weight distribution curve, when compared to the other known branched polymers such as those described in U.S. Patent 3,281,383, issued to Zelinski et al. Oct. 25, 1966 which do not show a plurality of modes and have a comparatively narrow molecular weight range. It should also be emphasized that the polymodal polymers of this invention possess other distinguishing properties over the known radial polymers such as improved processability and articles formed therefrom possess outstanding impact strength, clarity and environmental stress cracking resistance. Although the polymodal polymers of this invention do have a broader molecular weight distribution over the other known radial polymers, it is not believed that the broader molecular weight distribution alone accounts for all of these distinguishing properties.

The polymodal branched block copolymers of this invention are characterized in that they possess a melt flow in the range of about 0.5 to 20.0 and generally one from about 1.0 to 5.0 as determined by ASTM D-1238-65T, condition G.

Formed articles from the polymodal branched block copolymers have a haze transmittance in the range of about 0 to 20 percent and generally from 0 to 10 percent as determined by ASTM Method D-1003-61, Procedure A. Said articles have a falling ball impact strength value in ft.-lbs. of at least 1.0 and generally about 5.0 to 16.0 ft.-lbs. and often greater when calculated according to the following procedure: A ball of known weight is dropped from various heights until a height is found where four out of four samples tested, such as cereal bowls, crack when struck by the falling ball. Next, a height is found where two out of four bowls crack and finally a height where no bowls crack. These heights versus the percent failures are plotted on probability scale paper and the best straight line is drawn between those three points. The point of intersection between the drawn line and the 50 percent line is called the F50 value. The F50 value in feet multiplied by the weight of the ball in lbs. provides the falling ball impact strength value in ft.-lbs.

Said polymers are further characterized in that articles formed therefrom have an environment stress cracking resistance value in days of at least 100 days at zero percent failure when determined according to procedure of Example II.

Illustrative of the foregoing discussion and not to be interpreted as a limitation on the scope thereof, the following examples are presented.

EXAMPLE I

Polymodal branched block copolymers were prepared according to this invention. For comparative and control purposes radial polymers produced according to U.S. Patent 3,281,383 were also prepared. The latter compounds are referred to as regular radial polymers and those produced according to our invention as polymodal or as polymodal branched block copolymers. Regular radial and polymodal polymers of similar melt flow were produced to provide good comparative testing.

A typical polymodal polymer was produced according to the following recipe:

POLYMODAL POLYMER PREPARATION

First charge:	Amount
Cyclohexane -----pounds--	16.0
Styrene -----grams--	1,050
n-Butyllithium -----do--	.65
Tetrahydrofuran (THF) -----cc's--	4.0
Initial temperature, 130° F.	
Polymerization time <30 minutes.	
10 Second charge:	
Cyclohexane -----pound--	1.0
n-Butyllithium -----grams--	1.8
Styrene -----do--	450.0
Initial temperature, 160° F.	
15 Polymerization time <1 hour.	
Third charge:	
Cyclohexane -----pound--	.5
Butadiene -----grams--	500
Initial temperature, 165° F.	
20 Polymerization time <1 hour.	
Fourth charge:	
Epoxol 9-5 ¹ in toluene solution (0.5 gram/cc.) -----cc's--	20
25 Cyclohexane -----pound--	.5
Initial temperature, 180° F.	

¹ Epoxidized linseed oil, commercial, approximately five functional groups per molecule.

The cyclohexane and THF were charged to a 5-gallon stirred reactor vessel first. The monomer and initiator were added in the order indicated in the recipe. The polymerizations were begun at the temperatures shown in the recipe and were not permitted to exceed 250° F. Polymerizations were allowed to continue until essentially completed before the subsequent charge was made. At the conclusion of the polymerization and coupling, the reactor was emptied into isopropyl alcohol and recovered. The dried polymodal polymer was conventionally treated with 2 parts by weight of polymer antioxidant per 100 parts by weight of polymer. The antioxidants employed were 1.5 parts Polygard HR¹ and 0.5 part BHT.²

Other polymodal branched block copolymers were prepared according to the foregoing procedure and the essential data representing the polymer preparation and properties thereof are reported in Table I.

Regular radial polymers were produced according to the following formula and procedure and all of the polymerization were allowed to continue until essential completion before the subsequent charge was made.

First charge:	Amount
Cyclohexane -----pounds--	17.0
Styrene -----grams--	1400
n-Butyllithium -----do--	2.6
Initial temperature, 130° F.	
Polymerization time <30 minutes	
Second charge:	
Cyclohexane -----pound--	.5
Butadiene -----grams--	600
Third charge:	
Epoxol 9-5 in toluene solution (.5 gram/cc.) -----cc--	20
65 Acylohexane -----pound--	600

modal polymer. Table I contains data for polymer preparation of other radial polymers and also represents comparative testing of the properties of the regular radial and the polymodal polymer.

¹ Tri(monylphenyl)phosphite containing 1% triisopropanolamine.

² 2,6-di-tert-butyl-4-methylphenol.

TABLE I.—POLYMODAL BRANCHED BLOCK COPOLYMER

Run No.	Preparation, styrene portion				Properties						
	1st charge		2d charge		Percent ²		Melt flow ⁴	Flex. mod., ⁵ p.s.i. $\times 10^{-3}$	Tensile, p.s.i. ⁶	Elong., percent ⁷	Falling ball impact, ft.-lbs. ⁸
	Weight percent ¹	n-Butyllithium ²	Weight percent ¹	n-Butyllithium ²	Styrene	Butadiene					
A ^a -----	60	0.05	40	0.45	80	20	2.7	305	4,740	12	1.0
B-----	60	0.05	40	0.70	80	20	3.6	300	4,220	31	1.4
C ^b -----	60	0.08	40	0.37	75	25	3.2	256	4,250	72	5.0
D ^b -----	70	0.06	30	0.40	75	25	2.4	252	4,210	113	16.6
E ^b -----	70	0.06	30	0.53	75	25	3.9	256	4,030	128	16.9
F-----	60	0.03	40	0.35	80	20	0.9	-----	-----	-----	1.8
G-----	70	0.03	30	0.50	80	20	1.1	-----	-----	-----	>5.0

Regular radial											
n-Butyllithium ²											
H-----	.10	85	15	4.2	314	4,760	6	<.04	-----	-----	-----
I-----	.13	75	25	4.4	220	4,040	15	0.15	-----	-----	-----
J-----	.13	70	30	3.3	201	3,300	11	0.24	-----	-----	-----
K-----	.09	80	20	2.1	-----	-----	-----	-----	-----	-----	0.85
L-----	-----	100	-----	1.8	-----	-----	-----	-----	-----	-----	<0.1

¹ Weight percentage of total styrene employed in polymer preparation.
² Parts by weight n-butyllithium per 100 parts by weight of styrene charged in that portion.

³ Weight percentage based upon total weight of all monomers employed.
⁴ Determined by ASTM D 1238-63T, Condition G, at 200° C. with 5 kg. weight.

⁵ Determined by ASTM D 790.

⁶ Determined by ASTM D 638.

⁷ Falling ball impact of injected molded bowls using a free falling steel ball (0.71 and 2.3 lbs.) dropped at varying heights. Values calculated from height of drop at 50 percent failures. Bowls are molded on a Model 75 B New Britain reciprocating screw injection molding machine. The bowl bowl is single cavity, center gated and gives a part weight of 40 grams. The nozzle diameter is $\frac{1}{4}$ inch and is a pressure operated type with back-flow type screw tip. The bottom of the bowl is 70 mils. Molding conditions are as follows:

Rear zone temp., ° F.-----	440
Front zone temp., ° F.-----	450
Mold temp., ° F.-----	125
Screw, r.p.m.-----	104
Injection pressure, p.s.i.-----	15,000
Hold pressure, p.s.i.-----	6,000
Injection time, sec.-----	2
Total cycle, time, sec.-----	38

Table I effectively demonstrates some of the outstanding properties and especially the surprising impact strength of the transparent polymodal branched block copolymers produced according to this invention.

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mils. A commercial cooking oil is placed in the containers and covered with a lid. The containers are aged in a refrigerator at 40° F. until a leak occurs. This data is reported in Table II.

TABLE II

Run Number		Styrene/ butadiene content (weight, percent)	Melt ¹ flow	Number containers started	Number failed	Total, days tested
A-----	Regular radial-----	75/25	3.0	10	6	160
B-----	Regular radial-----	70/30	3.1	6	3	148
C-----	Regular radial-----	65/35	3.6	6	5	1
D-----	Regular radial-----	80/20	2.8	6	0	139

¹ As reported in Table I.

² Containers still being tested.

EXAMPLE II

Environmental stress cracking resistance tests were conducted upon thermoformed containers filled with a commercial cooking oil to determine the effectiveness of the polymodal block copolymers of this invention in resisting environmental breakdown. Polymer resistance to oil-based products, such as food, etc., is essential for actual consumer use and zero failures of a container is therefore necessarily required. The regular radial polymers were also tested for comparison. All of the polymers were prepared as in Example I to provide regular radial and polymodal polymer samples of similar melt flow.

The containers employed were prepared according to following description. A sheet, 30 mils thick, is extruded with a $1\frac{1}{2}$ Davis standard extruder, a 17 inch Goulding sheet die, and Goulding sheet line. The polymer temperature is 380 to 400° F. A light nip is used on the take-up rolls. The sheet is formed into food tubs with a Comet Labmaster Model L5 thermoformer. The containers are round with a depth at the center of about 1½ inches and I.D. at the top of about 4½ inches. The bottom of the formed tub is 15 to 20 mils and the side walls are 10 to 15

55

60

65

Table II effectively demonstrates the superiority of the polymodal branched block copolymers produced according to this invention as to their environmental stress cracking resistance.

EXAMPLE III

Tests were conducted to illustrate the outstanding clarity of the polymodal branched block copolymers of this invention. The polymers were prepared as in Example I and the polymer properties are reported in Table III. The percentage haze of the regular radial polymer and several commercial resins are reported for comparative purposes.

The haze of a specimen is that percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering. The percent haze was determined on 10 mil compression molded slabs according to ASTM Method D1003-61, Procedure A, using a Hazemeter. Only light flux deviating more than 2.5 degrees on the average was considered to be haze. The percentage haze is calculated as follows: Haze, percent = $T_d/T_i \times 100$ where T_d = diffuse transmittance and T_i = total transmittance. Although haze is a

75

comparative term because it depends on molding conditions and the thickness of the sample, the polymer samples employed in this example were molded under identical conditions to 10 mil slabs to insure unbiased ratings.

tion (Krueger HAK-1 pads). Flow rate was about 1 ml. per minute at room temperature through a four column array in series in the porosity order of 10^7 , 10^8 , 10^4 , and 10^3 angstroms.

TABLE III.—POLYMODAL BRANCHED BLOCK COPOLYMERS

Preparation, styrene portion					Properties				
Run No.	1st charge		2nd charge		Weight percent THF ²	Styrene ¹	Buta- diene ¹	Melt flow ¹	Percent haze ¹
	Weight percent ¹	n-Butyl- lithium ¹	Weight percent ¹	n-Butyl- lithium ¹					
A.....	60	0.03	40	0.38	0	80	20	1.1	3.2
B.....	60	.05	40	0.60	0	80	20	4.6	3.0
C.....	70	.06	30	0.43	0.10	78	22	2.0	2.0
D.....	70	.06	30	0.53	0.10	75	25	3.0	2.5
Regular radial									
N-Butyllithium (phm.) ⁴									
E.....		0.10				85	15	3.4	5.0
F.....		0.13				70	30	2.6	5.0
G.....		0.10				75	25	2.4	2.5
Commercial resins									
Trade name (supplier)					Type of polymer				
H.....	Styron 700 (Dow).....				Polystyrene.....				2.5
I.....	Type 20-D (Foster Grant).....				do.....				2.2
J.....	Tanite (Eastman).....				Cellulose acetate.....				4.5
K.....	XT-250 (Cyanamid).....				Acrylic multipolymer.....				4.5

¹ As reported in Table I.

² Weight percent THF based on total weight of monomers.

³ Percentage haze determined from 10 mil compression molded slabs according to ASTM method D 1003-61, procedure H, employing a Hazameter.

⁴ Parts by weight per 100 parts by weight total monomer.

From the foregoing data it is apparent that the clarity of the polymers of our invention, when compared to other known polymers of equivalent metal flow, is definitely superior or equal thereto. The degree of clarity, i.e., the lack of haze of the polymodal polymers of this invention is truly surprising especially when one considers the polymers employed as controls and further in view of the already demonstrated strength characteristics of the polymodal branched block copolymers.

EXAMPLE IV

The following example is presented to illustrate the polymodal nature of the polymers of our invention. Gel permeation chromatograph curves demonstrating the molecular weight distribution of the polymodal branched block copolymers is presented as well as is data for the regular radial polymers of the prior art. A gel permeation chromatographic curve (GPC) is reported for each polymer portion prepared after each step in the polymerization process, i.e., following completion of each step according to the process of this invention a polymer sample was withdrawn and a GPC curve made therefor. The heterogeneity index (HI) is reported as well. The heterogeneity index (HI) is employed as a synonymous expression for polydispersity and is the ratio of M_w/M_n ,¹ when this ratio is obtained by gel permeation chromatography. This ratio has a theoretical minimum value of 1. A polymer possessing a ratio of 1 is said to be monodispersed. The broadness of the molecular weight distribution, or polydispersity, is thus reflected by the value of this ratio, i.e., the larger the HI number, the broader the molecular weight distribution, or the greater the polydispersity.

Gel permeation chromatograms were obtained using a Waters Associates Model 100 GPC utilizing polystyrene gel packed columns of the best available quality. Polymer solutions were prepared to 0.05 weight volume percent in tetrahydrofuran. Sample size was 2 mls. of filtered solu-

A polymodal branched block copolymer was prepared according to the following polymerization procedure. To a three-liter stirred reactor was charged 0.5 pound of cyclohexane solvent at a reactor temperature of 164° F. 108.0 grams of styrene monomer was then charged and 0.3 pound of cyclohexane solvent. 4.3 grams of a 1.0 weight percent n-butyllithium solution and 0.2 pound of cyclohexane solvent were charged and the reaction mixture was allowed to polymerize for 20 minutes. Following essentially complete polymerization of the styrene monomer an additional 28.8 grams of 1.0 weight percent n-butyllithium solution and 0.2 pound of cyclohexane, 72.0 grams of styrene monomer and 0.3 pound of cyclohexane was added to the reactor and styrene allowed to polymerize for an additional 20 minutes. Butadiene monomer was then added and polymerized for 20 minutes. Following the butadiene polymerization, 2.3 ccs. of Epoxyl 9-5 in a toluene solution containing 0.5 gram of Epoxyl 9-5 per cc. of solution, 0.5 weight percent Epoxyl 9-5, based upon the total weight of monomer employed in the polymer preparation, was added and allowed to react for 10 minutes. Following the Epoxyl 9-5 reaction, the polymer solution was precipitated by addition to isopropyl alcohol (about equal volume of alcohol to polymer solution). The precipitated polymer was separated from the alcohol and solvent and dried in a vacuum at 160-212° F. for 30-60 minutes. The dried polymer was chopped in a polymer grinder and treated with two parts of antioxidant per 100 parts of total polymer. The antioxidant employed was Polygard HR, 1.5 parts and BHT 0.5 part per 100 parts of total monomer. The stabilized polymer was redried in a vacuum oven until a constant weight was obtained. FIGS. 1(a) through 1(d) represent the gel permeation chromatographic curves obtained in the preparation of the polymodal branched block copolymer.

FIG. 1(a) represents the GPC curve of the polymer sample obtained following the polymerization of the first styrene addition wherein 0.04 part by weight of n-butyllithium per 100 parts by weight of styrene was employed.

FIG. 1(b) represents the GPC curve for the polymer sample obtained after the polymerization of the second

¹ A commonly employed method of expressing the molecular weight distribution is in the form of a ratio M_w/M_n , wherein M_w equals the weight average molecular weight and M_n equals the number average molecular weight.

portion of the styrene wherein 0.4 part by weight of n-butyllithium was employed per 100 parts by weight of styrene charged in that portion. The second styrene charge represents 40 percent of the total styrene monomer employed. FIG. 1(c) represents the GPC curve of the polymer sample obtained after the butadiene has been polymerized onto the polystyrene segments previously formed to produce the block copolymer.

FIG. 1(d) represents the GPC curve for the complete polymodal branched block copolymer of this invention.

The polymer samples represented in FIGS. 1(a) to 1(d) possessed the following properties:

Figure	Melt flow	Inherent viscosity	M _w	M _n	HI
1(a)-----	1.6	0.83	251,000	213,000	1.18
1(b)-----	9.4	0.58	161,000	47,000	3.4
1(c)-----	17.3	0.87	142,000	59,000	2.4
1(d)-----	1.3	0.80	217,000	108,000	2.1

The polymodal nature of the polymers of this invention are therein clearly depicted. The relatively high heterogenic index and relatively low melt flow are excellent supportive evidence for the excellent polymer processability of the polymodal branch block copolymers of this invention which is hereinafter demonstrated.

A regular radial polymer was prepared under like conditions and GPC curves obtained on the final radial polymer and on the polymer samples taken from each step in the polymerization process. The regular radial polymer was prepared according to the following polymerization conditions. To a three-liter stirred reactor was charged 1.2 pounds of cyclohexane solvent at room temperature. The reaction temperature was increased to 140° F. and 180 grams of styrene monomer and 0.3 pound of cyclohexane solvent were charged. 18.0 grams of 1.0 weight percent n-butyllithium in solution and 0.3 pound of cyclohexane solvent were added to the reactor. The reaction temperature was 141° F. The styrene monomer was allowed to polymerize for 25 minutes and the maximum temperature reached was about 180° F. Following the styrene polymerization, 45.0 grams of butadiene and 0.3 pound of cyclohexane solvent were added at a reaction temperature of about 149° F. The butadiene was allowed to polymerize for 25 minutes and 2.3 ccs. of Epoxyl 9-5 in toluene containing 0.5 gram of Epoxyl 9-5 per cc. of solution and 0.5 pound of cyclohexane solvent were added. The Epoxyl 9-5 was charged at a reactor temperature of 150° F. and allowed to react for 10 minutes. Following the Epoxyl 9-5 reaction, the polymer solution was precipitated and recovered and treated according to the same procedure as employed for the polymodal branch block copolymer. FIG. 2(a) illustrates the GPC curve of the polymer sample obtained following the polymerization of the first styrene charge and was produced with 0.10 part of n-butyllithium per 100 parts of styrene monomer by weight. FIG. 2(b) represents the GPC curve of the polymer sample obtained following the polymerization of the butadiene charge to form the styrene/butadiene block copolymer. The butadiene was present in an amount to provide 20 weight percent butadiene of the total weight of the polymer.

FIG. 2(c) represents the final radial polymer produced, i.e., after coupling with the polyfunctional treating agent Epoxyl 9-5. The polyfunctional treating agent was charged in an amount to provide 0.5 weight percent of treating agent per total weight of monomers employed. Epoxyl 9-5 was employed in a toluene solution containing 0.5 gram of Epoxyl 9-5 per cc. of solution. The polymer samples represented in FIGS. 2(a) to 2(c) possessed the following properties:

Figure	Melt flow	M _w	M _n	HI
2(a)-----	55.0	76,000	65,000	1.17
2(b)-----	14.0	95,000	82,000	1.16
2(c)-----	1.6	179,000	132,000	1.35

The absence of the polymodal configuration of the GPC curve when compared to the GPC curve of the polymodal branch block copolymer is evident. Although the melt flow of the regular radial is very nearly that of the polymodal branch block copolymer, the lower heterogenic index is apparent. It is clear from the foregoing GPC data that there exists many distinguishing features between the polymodal branch block copolymers of this invention and the prior art branched polymers.

EXAMPLE V

The following example is presented to illustrate the outstanding processing properties of the polymodal branch block copolymers of this invention. Polymers possessing various outstanding properties of strength, clarity, etc., are of little value unless the polymer can be easily processed and employed in conventional equipment. The resinous polymers are obviously required to undergo flow in the molten state during the course of manufacture and fabrication of products and the important processing operations such as extrusion, molding, calendaring, etc., all involve the behavioral flow of the molten or relatively fluid polymer.

Table IV contains data illustrating that the polymodal polymer of this invention flows better for a given set of conditions than the regular radial polymers. The higher the value for the injected molded spiral flow data, i.e., the better the flow and processability.

Run number	Type of polymer	Percent butadiene ²	Melt flow ³	Spiral flow ⁴
1-----	Regular radial ¹	15	3.4	9.7
2-----	do ²	25	3.1	8.9
3-----	do ¹	30	2.6	9.8
4-----	Multiple addition ¹	20	2.9	14.1
5-----	do ²	20	2.4	13.7

¹ Prepared as in Example I.

² Prepared as in Example I except polyfunctional treating agent silicon tetrachloride at 0.10 part by weight per 100 parts by weight total monomer.

³ As reported in Table I.

⁴ Spiral flow determined from injection mold in inches at 410° F. at 17,000 p.s.i.

Melt flow characteristics of the polymodal polymers of this invention and the regular radial polymers as shown by CIL data (Canadian Industries, Limited) obtained at 200° C., according to ASTM D-1703-62 are shown in FIG. 3.

A log-log plot of melt viscosity versus shear rate in reciprocal seconds is reported in FIG. 3. The shear rate, a function of the size of the hole and the pressure used to force the polymer through said hole, and the melt viscosity are calculated according to ASTM D-1703-62. In general, the lower the melt viscosity for any given shear rate, the better the processability of the polymer especially for high speed injection molding, wire coating, and the like. Also, the steeper the slope, the better the shear response and the better the processability for the above high speed applications.

The regular radial polymers represented in FIG. 3 were produced according to Example I. The regular radial polymer designated (A) had a melt flow of 3.0, regular radial, (B) had a melt flow of 9.0. Polymodal polymers of this invention are represented by Run C with a melt flow of 3.0. It is therein also demonstrated that the polymodal polymers flow better at these conditions than a 9.0 melt flow regular radial polymer. The steeper slope of the CIL curve for the polymodal polymer indicates that these polymers exhibit increased shear response over the regular radial polymers. This means that the polymodal polymers respond better to increased shear rates and flow faster.

The injection molded spiral flow data and the CIL data correlate very well and demonstrate that the polymodal polymers of this invention possess improved processing characteristics.

Summarily, the novel resinous polymodal branched block copolymers produced according to the process of this invention possess a combination of properties including excellent processability and articles formed therefrom

exhibit outstanding transparency, environmental stress cracking resistance, and impact strength. The combination of these properties in a single polymer represents a significant advancement in the polymer field.

As will be evident to those skilled in the art, various modifications of this invention can be made or followed in light of the disclosure and the discussion herein set forth without departing from the scope or the spirit thereof.

We claim:

1. A resinous radial polymer comprising from about 70 to 95 weight percent polymerized monovinyl-substituted aromatic hydrocarbon monomer containing from about 8 to 18 carbon atoms per molecule and from about 30 to 5 weight percent polymerized conjugated diene monomer containing from about 4 to 12 carbon atoms per molecule; said polymer having a melt flow in the range of about 0.5 to 20.0 as determined by ASTM D-1238-65T, condition G; copolymer branches forming said radial configuration being at least three in number and further being of a block configuration; said branches being of polymer demonstrating a plurality of modes on a gel permeation chromatograph curve prior to coupling with a polyfunction agent to produce said polymer; said polymer when formed into articles demonstrating a haze transmittance in the range of about 0 to 20 percent as determined by ASTM D-1003-61, Procedure A, a falling ball impact strength value in ft.-lbs. of at least 1.0 and environmental stress-cracking resistance value in days of at least 100 days at zero percent failure.

2. The polymer of claim 1 wherein said polymer comprises from about 75 to 85 weight percent polymerized monovinyl-substituted aromatic hydrocarbon monomer and from about 25 to 15 weight percent polymerized conjugated diene monomer, said polymer having a melt flow in the range of about 1.0 to 5.0, said polymer when formed into articles demonstrating a haze transmittance in the range of about 0 to 10 percent and a falling ball impact strength value of at least 5 to 16.

3. A polymerization process for preparing resinous branched block copolymers comprising the sequential steps:

(a) contacting under polymerization conditions at a temperature up to about 250° F. a monovinyl-substituted aromatic hydrocarbon monomer containing from about 8 to 18 carbon atoms per molecule with an organolithium polymerization initiator containing from about 1 to 20 carbon atoms per molecule wherein said monovinyl-substituted aromatic hydrocarbon monomer is employed in an amount to provide from about 40 to 90 weight percent of the total monovinyl-substituted aromatic hydrocarbon employed in preparing said copolymer wherein said initiator is employed in an amount to provide from about 0.01 to 0.2 part by weight of initiator per 100 parts by weight of said monomer and continuing said contacting for a period of time sufficient to polymerize essentially all of said monovinyl-substituted aromatic hydrocarbon monomer;

(b) charging to the polymerization reaction product of step (a), in one or more increments, the remaining monovinyl-substituted aromatic hydrocarbon monomer representing from about 10 to 60 weight percent of said total monovinyl-substituted aromatic hydrocarbon monomer employed in preparing said copolymer; wherein for each incremental charge of monovinyl-substituted aromatic hydrocarbon monomer additional said organolithium initiator is provided in an amount from about 0.1 to 1.5 parts by weight of said initiator per 100 parts by weight of said incremental charge of monomer, wherein after each monomer and initiator charged a sufficient contacting time is allowed to permit essentially complete polymerization of the newly added monomer, wherein the amount of initiator employed per 100 parts by weight

of each incremental monomer charge of step (b) exceeds the amount of initiator employed in step (a) by at least 0.1 part of initiator per 100 parts of monomer by weight and wherein the total amount of said monovinyl-substituted aromatic hydrocarbon monomer employed in steps (a) and (b) comprises from about 70 to 95 weight percent of the total weight of said branched block copolymer based upon the total weight of all of the monomers employed;

(c) charging to the polymerization reaction product of step (b) a conjugated diene monomer containing from about 4 to 12 carbon atoms per molecule and polymerizing to essential completion said diene monomer in the presence of said reaction product to form a block copolymer, and wherein the amount of said diene monomer comprises from about 30 to 5 weight percent of the total weight of said branched block copolymer based upon the total weight of all of the monomers employed; and

(d) charging to the polymerization reaction product of step (c) a polyfunctional treating agent capable of reacting with terminal lithium atoms on a preformed polymer to form a branched polymer wherein said polyfunctional treating agent is employed in an amount to provide from about 0.05 to 2 equivalents of said polyfunctional treating agent per gram atom of lithium employed in said polymerization process.

4. The polymerization process of claim 3 wherein said contacting under polymerization conditions is at a temperature below about 230° F., wherein the amount of monovinyl-substituted aromatic hydrocarbon monomer employed in step (a) is at least 60 weight percent of the total monovinyl-substituted aromatic hydrocarbon monomer employed in preparing said copolymer, wherein said initiator employed in step (a) is in an amount to provide from about 0.03 to 0.10 part by weight of initiator per 100 parts by weight of said monomer, wherein the amount of monovinyl-substituted aromatic hydrocarbon monomer employed in step (b) is less than 40 weight percent of said total monovinyl-substituted aromatic monomer employed in preparing said copolymer, wherein from about 0.3 to 1.5 parts by weight of said initiator per 100 parts by weight of said incremental charge of monomer is employed in step (b), wherein the amount of initiator employed per 100 parts by weight of each incremental monomer charged (s) of step (b) exceeds the amount of initiator employed in step (a) by at least 0.2 part of initiator per 100 parts of monomer by weight, wherein said conjugated diene monomer is employed in an amount to provide from about 25 to 15 weight percent of the total weight of said branched block copolymer based upon the total weight of all of the monomers employed, and wherein from about 0.5 to 1.5 equivalents of said polyfunctional treating agent is employed per gram atom of lithium employed in said polymerization process, and wherein said initiator can be represented by the formula RLi wherein R is a hydrocarbon radical selected from aliphatic, cycloaliphatic, or aromatic radicals containing from about 1 to 20 carbon atoms per molecule.

5. The process of claim 3 wherein said contacting step (a) includes the addition of .005 to 5 weight percent of tetrahydrofuran based on the total amount of monomer employed in preparing said branched block copolymer.

6. The process of claim 4 wherein said contacting step (a) includes the addition of about .05 to .1 weight percent of tetrahydrofuran based on the total weight of monomer employed for preparing the branched block copolymer.

7. The process of claim 3 wherein said polyfunctional treating agent contains at least three functional groups capable of reacting with terminal lithium atoms on a preformed polymer and said polyfunctional treating agent is selected from the polyepoxides, the polyamines, the polyisocyanates, polyaldehydes, polyhalides, polyketones, or tin compounds.

8. The process of claim 3 wherein said polyfunctional treating agent is epoxidized linseed oil, said initiator is n-butyllithium, said conjugated diene is butadiene and said monovinyl-substituted aromatic hydrocarbon is styrene.

9. The process of claim 3 wherein said polyfunctional treating agent is a difunctional treating agent, said agent being a monomeric material capable of addition to itself.

10. The process of claim 4 wherein said polyfunctional treating agent is selected from silicon tetrachloride, tetraallyltin, stannic fluoride, or epoxidized linseed oil.

11. An article of manufacture comprising the resinous polymer of claim 1.

12. The process of claim 3 wherein step (b) comprises charging said organolithium initiator to the reaction prod-

uct of step (a) prior to charging said incremental charge of monomer.

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Kitchen

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[54] **COUPLED RESINOUS DIENE COPOLYMER
WITH GOOD INTEGRAL HINGE FLEX LIFE
AND HIGH HARDNESS**

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[21] Appl. No.: 699,731

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[51] Int. Cl.² C08F 297/04

[52] U.S. Cl. 260/880 B

[58] Field of Search 260/880 B

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Primary Examiner—Paul R. Michl

[57] ABSTRACT

A conjugated diene/monovinyl-substituted aromatic compound resinous copolymer such as a styrene/-butadiene block copolymer is produced using two additions of the monovinyl-substituted aromatic component and initiator in a manner such that the product has 71 to 81 wt. percent monovinyl-substituted aromatic component and has a ratio based on the number average molecular weight of monovinyl-substituted aromatic component blocks in first and second polymer chains thus produced prior to coupling within the range of 3 to 7. The final product resulting from coupling such polymers has long integral hinge flex life and high hardness. This is accomplished by using no more than 5 millimoles of initiator per mole of monomer in the second addition.

15 Claims, No Drawings

COUPLED RESINOUS DIENE COPOLYMER WITH GOOD INTEGRAL HINGE FLEX LIFE AND HIGH HARDNESS

BACKGROUND OF THE INVENTION

This relates to resinous coupled block copolymers.

It is known to produce block copolymers by the sequential addition of monomers such as styrene and butadiene. It is further known to produce a completely different class of these block copolymers wherein the monovinyl-substituted aromatic compound and initiator are added in two or more increments prior to addition of the conjugated diene and the resulting diblock chains having varying styrene block links are thereafter coupled with a polyfunctional coupling agent.

As is generally the case, the properties of the resulting polymers can be varied by varying the polymerization technique. For instance, if a more flexible material is desired, a smaller amount of monovinyl-substituted aromatic component and a larger amount of conjugated diene can be utilized, but this of course results in sacrificing other properties such as hardness.

SUMMARY OF THE INVENTION

It is an object of this invention to produce a coupled copolymer having both high flex life and good hardness.

In accordance with this invention, a resinous monovinyl-substituted aromatic compound/conjugated diene copolymer is produced using multiple addition of monovinyl-substituted aromatic compound and initiator to give a product having 71 to 81 weight percent monovinyl-substituted aromatic compound with a ratio based on the calculated number average molecular weight of monovinyl-substituted aromatic compound block in the chains produced by the first and second addition of initiator and monovinyl-substituted aromatic compound within the range of 3 to 7.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The production of resinous branched block copolymers is broadly disclosed in Kitchen et al. U.S. Pat. No. 3,639,517 issued Feb. 1, 1972, the disclosure of which is hereby incorporated by reference. The instant invention represents an improvement over the basic disclosure of Kitchen et al in the provision for a ratio of number average molecular weight of the monovinyl-substituted aromatic compound blocks in the polymer produced by the first and second initiator additions within the range of 3 to 7 as will be described in detail hereinbelow.

The applicable monovinyl-substituted aromatic component monomers, conjugated diene monomers, and initiators are identical to those disclosed in said Kitchen et al patent as is the polymerization procedure, except as specifically noted hereinbelow.

Briefly, polymerization involves the first addition of a monovinyl-substituted aromatic component monomer such as styrene along with an organolithium initiator to produce a group of monovinyl-substituted aromatic component polymer blocks terminated with lithium atoms followed by the introduction of additional initiator and additional monovinyl-substituted aromatic compound monomer so as to produce a second group of monovinyl-substituted aromatic component polymer blocks also terminated with lithium atoms. Thereafter, the conjugated diene monomer is introduced to form

chains consisting of monovinyl-substituted aromatic component-diene blocks terminated with lithium atoms having varying lengths because of the multiple addition of the monovinyl-substituted aromatic compound monomer and initiator. Thereafter, a polyfunctional coupling agent having at least 3 functional groups per molecule is employed to join together a plurality of these chains so as to form polymer molecule having terminal polymerized monovinyl-substituted aromatic component blocks.

Providing the necessary favorable polymerized monovinyl-substituted aromatic compound block sequences to achieve substantially greater hinge flex life while retaining good physical properties and Shore D hardness values of about 73 or greater forms the basis of this invention.

Substantially greater hinge flex life in the context of this invention means total cycles ranging from about 650 to about 1,000 or greater for polymers having a 71 to 77 weight percent monovinyl-substituted aromatic compound content and 200 to 650 for those having a 78 to 81 weight percent monovinyl-substituted aromatic compound content. Articles having integral hinges molded from branched block copolymers of the same monovinyl-substituted aromatic compound content but which are not within the specific ratios of monovinyl-substituted aromatic content block length in the two groups of blocks (conventional branched block copolymers) exhibit much lower flex life. The thickness of the hinges of the test samples used establish the above values was about 0.020 inches (0.05 cm) in all instances. Samples having differing hinge thicknesses would be expected to show somewhat different results. However, the relative improvement for the invention polymers compared with conventional polymers is expected to be about the same regardless of the hinge thickness.

Conventional branched block copolymers containing about 76 wt. % polymerized styrene for instance have a Shore D hardness of about 69 whereas invention polymers containing the same wt. % polymerized styrene have Shore D hardness values of about 73 to 75 as well as improved integral hinge flex life. It is desirable that the molded articles have as high a hardness value as possible to reduce marring or scratching which can be incurred during use.

Regulation of the molecular weight of the polymerized monovinyl-substituted aromatic compound blocks in the radial polymers of this invention is achieved by the amount of initiator employed during polymerization. Good results are obtained when using two portions of styrene by using styrene weight ratios, portion one to portion two, ranging from about 1:1.5 to 2:1 preferably 1:1 to about 1.9:1. Good results are obtained with weight ratios of portion one to portion two of initiator ranging from about 0.5:1 to about 1.5:1, preferably 0.67:1 to 1:1.

The polymers of this invention are further characterized as follows: The styrene content in the relatively high molecular weight diblock polymer chains produced by the first addition of monomer and initiator and conjugated diene addition is calculated to be less than 90 weight percent, preferably 80 to 89, more preferably 84 to 85 weight percent. The polymerized styrene content in the relatively low molecular weight diblock polymer chains produced as a result of the second addition of monomer and initiator and conjugated diene addition is greater than 46 weight percent, preferably 47 to 70, more preferably 49 to 67 weight percent.

The ratio of the calculated number average molecular weight of the styrene block in the high and low molecular weight portions (portions resulting from the first and second initiator and styrene additions, respectively) is 3 to 7, preferably 3.5 to 4.8. The ratio of the calculated number average molecular weight of the total monovinyl-substituted aromatic compound-diene block of the high and low molecular weight portions respectively, is less than 4.5, preferably 2 to 4, more preferably 2.5 to 3.3.

The copolymers have a total weight percent monovinyl-substituted aromatic compound content within the range of 71 to 81, more preferably 75 to 77, most preferably about 76 weight percent.

These combinations of properties are achieved by utilizing a content of initiator in the first addition within the range of 2.0 to 2.7, preferably 2.14 to 2.57 millimoles per mole of monomer in that addition and an amount of initiator in the second addition within the range of 3 to 5, preferably 3.66 to 4.93 millimoles of initiator per mole of monovinyl-substituted aromatic compound monomer in that addition.

EXAMPLE

The control resins were prepared as broadly described in the previously mentioned Kitchen et al patent. The invention runs were prepared using relatively more initiator in the first addition and relatively less in the second.

The polymers were prepared in a 5 gallon (0.019 m³) stirred reactor according to the following general charge order:

Cyclohexane containing 0.025 parts by weight per 100 parts by weight monomer (PHM) tetrahydrofuran (THF).

Styrene, first portion.

n-Butyllithium solution, first portion, about 10 wt. % in cyclohexane.

n-Butyllithium solution, second portion.

Styrene, second portion

Conjugated diene.

Epoxidized soybean oil solution (0.50 g oil/cc cyclohexane).

Water, 0.2 PHM.

CO₂, 0.1 PHM.

Antioxidant in cyclohexane solution.

About 93 weight percent of the total cyclohexane containing 0.025 parts by weight THF per 100 parts by weight monomer (PHM), was preheated to about 100° F (38° C) and charged to the reactor. The remaining cyclohexane was consumed as a diluent or flush for the portions of monomers subsequently added to the reactor. It is essential to have two separate charges of styrene and initiator. The exact mode of adding each of these two charges of styrene can vary, however. The simplest procedure is simply to add all of the first charge at one time and all of the second at one time. Alternatively one or both can be added continuously or incrementally. The advantage of incremental addition, particularly of the charge associated with the second initiator addition is to limit the peak temperature resulting from each addition to below about 180° F (82° C) which has been found to be desirable in this process. The procedure actually used in this example is as follows. After charging the cyclohexane, the first portion of styrene was charged and then the first portion of n-butyllithium initiator. Then the second portion of initiator was charged and the second portion of the

styrene monomer. The first styrene portion and the second styrene portion were allowed to polymerize about 10-20 minutes. The peak temperatures reached during styrene polymerization ranged from about 160° to about 175° F (71°-79° C) for the various runs. The conjugated diene, preferably 1,3-butadiene, or conjugated dienes, if more than one was used (the second being isoprene) was then charged. Each diene was charged separately in one increment. Total polymerization time for diene(s) amounted from about 20-40 minutes and the peak temperatures reached averaged about 214° F (101° C). Following polymerization of the diene charge, while the polymer cement remained at about 214° F, a solution of epoxidized soybean oil amounting to 0.5 PHM was added. A time of about 20 minutes was allowed for the coupling reaction to take place. The solids content in the reactor at this time averaged about 30-35%. The epoxidized soybean oil had a molecular weight of about 1,000 and contained about 4 epoxy groups per formula weight. Following the coupling reaction, the polymer solution was contacted with about 0.2 PHM water and about 0.1 PHM CO₂ for about 10 minutes while still at coupling temperature. Thereafter, the antioxidant solution was added to the reactor and mixed with the contents. The resin was recovered by heating the contents to about 315°-330° F (157°-166° C) and flashing off the solvent.

A stabilizer system consisting of either about 1.5 PHM tris(nonylphenyl) phosphite and about 0.5 PHM 2,6-di-t-butyl-4-methylphenol (BHT) or about 0.5 PHM BHT and about 1.5 PHM Geltrol was used to impart stability to the polymers. Geltrol is a glycine having the formula



wherein R is either a C₁₄, C₁₆, or C₁₈ alkyl group. An example is: N-octadecyl-N'-(carboxymethyl)-trimethylene diglycine. These compounds are disclosed in 121,2566 *Federal Register*, Dec. 20, 1969, 34 F.R. 19972, subpart F — Food Additives — pages 62 and 62.1, respectively. While 1.5 PHM was used in the Examples in conjunction with about 0.5 PHM BHT, it is also possible to use this stabilizer in conjunction with both a sterically hindered phenol and an organic phosphite. In such instances, the glycine will be present in an amount within the range of 1 to 50, preferably 25 to 37 weight percent based on the weight of the phosphite. The total amount of phosphite and glycine in the polymer will be within the range of 0.2 to 5, preferably 0.5 to 2 weight percent of this mixture based on the weight of the polymer. The phenol will be present in an amount within the range of 0.05 to 5, preferably 0.1 to 1 weight percent based on the weight of the polymer.

A listing of the quantities of initiators and monomers used, the block sequence for each resin, calculated number average molecular weights and calculated ratios for the high molecular weight blocks to low molecular weight blocks are presented in Table I. The molecular weights are calculated assuming a zero poison level, for convenience.

Selected physical properties for the polymers of Table I are presented in Table IA. The polymers of Table IA, identified by each run number, correspond to those of Table I with the same numerical run number.

Test specimens for determination of integral hinge life were prepared by injection molding at a melt temperature of about 425° F (218° C) and an injection pressure of about 6,000 to about 8,000 psi (41.4 – 55 MPa). Each specimen was about 3.5 inches long (8.9 cm), 1 inch wide (2.5 cm) and 0.08 inches thick (0.2 cm). A V-shaped depression, rounded at the top and bottom,

about 0.02 inches (0.05 cm). Each specimen was clamped flush with the hinge and evaluated for flex life by flexing the hinge 180° with a stress of 1.5 kg in a Tinius Olsen Folding Endurance Tester at the rate of about one cycle per second until the hinge failed. The hinge life shown in Table IA represents the average of 10 specimens tested per polymer sample.

Table I

Run No.	Polymerization Details and Calculated Properties					
	1	2	3 ⁽¹⁾	4	5	6
Styrene, PHM 1st addition	56	40	58	57	53	38
Styrene, PHM 2nd addition	24	40	20	19	23	38
NBL, 1st addition ⁽²⁾	0.872	2.44	1.06	0.942	1.01	2.55
NBL, 2nd addition ⁽²⁾	7.45	3.66	9.79	9.84	8.51	3.86
Diene, PHM						
Butadiene	20	20	22	24	24	24
Isoprene	0	0	0	0	0	0
Block Sequence						
Before Coupling	S-B	S-B	S-B	S-B	S-B	S-B
Calculated Molecular Weight						
Polystyrene						
from 1st addition	131,910	64,350	104,730	117,770	103,400	67,100
from 2nd addition	10,900	18,170	8,060	8,200	9,420	17,550
HMW ⁽³⁾ S-D Block	140,000	73,420	113,600	128,080	113,300	77,780
LMW ⁽⁴⁾ S-D Block	20,000	27,270	16,940	18,560	19,250	28,620
S/D Ratio						
HMW Portion	94/6	88/12	92/8	92/8	91/9	86/14
LMW Portion	54/46	67/33	48/52	44/56	49/51	61/39
Block Ratios, High/Low ⁽⁵⁾						
Polystyrene Only	12.1	3.5	13.0	14.4	10.9	3.8
S/D	7.0	2.7	6.7	6.9	5.9	2.7
Remarks	Control	Invention	Control	Control	Control	Invention
Run No.	7	8	9	10	11	
Styrene, PHM 1st addition	38	45.6	53	53	38	
Styrene, PHM 2nd addition	38	30.4	23	23	38	
NBL, 1st addition ⁽²⁾	2.57	2.14	2.14	0.859	2.57	
NBL, 2nd addition ⁽²⁾	3.86	4.83	4.93	7.78	3.86	
Diene, PHM						
Butadiene	24	24	24	19	19	
Isoprene	0	0	0	5	5	
Block Sequence						
Before Coupling	S-B	S-B	S-B	S-I-B	S-I-B	
Calculated Molecular Weight						
Polystyrene						
from 1st addition	57,000	61,890	58,440	132,920	57,000	
from 2nd addition	16,290	13,020	10,410	10,620	16,290	
HMW ⁽³⁾ S-D Block	67,290	72,140	69,310	144,000	67,290	
LMW ⁽⁴⁾ S-D Block	26,570	23,300	21,280	21,690	26,570	
S/D Ratio						
HMW Portion	85/15	86/14	84/16	92/8	85/15	
LMW Portion	61/39	56/44	49/51	49/51	61/39	
Block Ratios, High/Low ⁽⁵⁾						
Polystyrene Only	3.5	4.8	5.6	12.5	3.5	
S/D	2.5	3.1	3.3	6.6	2.5	
Remarks	Invention	Invention	Invention	Control	Invention	

⁽¹⁾Total monomer weight equaled 2500 grams in Runs 3 and 4, 2900 grams in Run 9, all other 30000 g.

⁽²⁾mmoles n-butyllithium per mole styrene in each styrene addition.

⁽³⁾polymerized high molecular weight styrene-diene block.

⁽⁴⁾polymerized low molecular weight styrene-diene block.

⁽⁵⁾Calculated number average molecular weight.

Table IA

Run No.	Physical Properties of Sample Resins							Remarks
	Melt Flow ^(a)	Hardness Shore D	Flexural Modulus ^(b) psi × 10 ⁻³	Flexural Modulus ^(b) MPa	Tensile Yield ^(c) psi	Tensile Yield ^(c) MPa	Elongation ^(c) %	
1	5.9	74	275	1896	4200	28.96	28	Control
2	8.8	75	242	1669	3880	26.75	10	Invention
3	5.5	75	238	1641	3280	11.31	164	Control
4	5.9	69	221	1524	3000	20.68	167	Control
5	5.8	71	230	1586	3270	11.27	144	Control
6	8.0	75	213	1469	3330	22.96	7	Control
7	7.2	74	215	1482	3570	24.61	12	Invention
8	8.2	74	215	1482	3600	24.82	6	Invention
9	7.6	73	215	1482	3730	25.72	7	Invention
10	5.2	69	232	1600	3110	11.03	150	Invention
11	8.8	74	227	1565	3420	23.58	11	Control

^(a)ASTM D1238-73, condition G

^(b)ASTM D790-71

^(c)ASTM D638-72, 0.2 inches/minute

extending across the entire width of the specimen was located about 0.4 inches (1 cm) from one end. The top width of the depression was about 0.16 inches (0.4 cm) and it was about 0.06 inches (0.15 cm) deep. Thus, the minimum thickness of the web forming the hinge was

Inspection of the data presented in the Tables shows a conventional branched block copolymer in control run 1 containing 80 weight percent polymerized styrene

with physical properties typical of such polymers. It possesses a hinge flex life of about 123 cycles and a Shore D hardness of 74. Invention runs 2 shows substantially higher values for flex life as a result of adjusting initiator levels to give a polymer having a ratio of block weights within the scope of this invention. Control runs 3 to 4 show that flex life can be improved by increasing the diene content as might be expected but at a sacrifice in hardness as would also be expected. The polymer of control run 5 represents a conventional branched block copolymer at what the prior art considered optimum conditions. This polymer has better flex life than control 1 but still at a sacrifice in hardness (71 versus 74). The invention polymers of runs 6 to 9 were prepared by either decreasing the first styrene charge and/or increasing the first initiator charge to the reactor. The effect is to reduce the number average molecular weights of the high molecular weight fractions from calculated values of about 120,000 to 150,000 in conventional branched block copolymers down to a value for the invention polymers of about 50 percent of that of the conventional polymers. In addition, the amount of initiator added in the preparation of the low molecular weight fractions is decreased relative to conventional polymerization procedure. The effect is to increase the calculated number average molecular weights of the low molecular weight fractions. Thus, the calculated polystyrene (or polystyrene-polydiene) ratios of the high molecular weight fractions to low molecular weight fractions ranges from 3.5 to 4.8 (2.5 - 3.3) for invention polymers contrasted with the 10.9-14.4 (5.9 - 6.9) for conventional polymers. The figures in brackets represent the calculated values for the corresponding polystyrene-polydiene block ratios. Thus, the low block MW ratios of the invention polymers are associated with high hinge flex life values. Control polymers exhibit high block MW ratios and substantially lower hinge flex life values.

Control 10 and invention run 11 show the same advantage when part of the butadiene is replaced with another diene, isoprene.

The calculation of the number average molecular weight is done based on the amount of initiator and monomer used and employs the assumption that there are no poisons present and that the initiation rate of the second initiator charge is the same as the propagation rate of the first. This is known in the art.

Table II hereinbelow summarizes selected data from Tables I and IA to better illustrate the invention.

Table II

	Styrene PHM		NBL, PHM		Diene, PHM	S/D Ratio HMW Portion	Polystyrene Block Ratio High/Low		Flex Life Cycle	Hardness, Shore D
	1st	2nd	1st	2nd						
1	56	24	0.030	0.110	20	94/6	20.8	123 control	74	
2	40	40	0.060	0.090	20	88/12	3.5	303 invention	75	
5	53	23	0.033	0.12	24	91/9	10.9	508 control	71	
9	53	23	0.070	0.070	24	84/16	3.6	929 invention	73	

As can be seen, run 1 representing a conventional branched block copolymer having 56 parts of styrene added in the first increment with 0.030 parts of initiator, 24 parts styrene in the second portion with 0.110 parts of initiator for a total polymerized styrene content of 80 wt percent and a total polymerized butadiene content of 20 wt percent gave a polymer with very poor flex life. Invention run 2 utilized the same total amount of styrene and butadiene, but compared with control run 1 less styrene and more initiator were used in the first

increment and more styrene and less initiator in the second so as to give a copolymer which had a polystyrene to polydiene weight ratio in the high molecular weight portions (portions resulting from the addition of the 40 parts of styrene and 0.060 parts of initiator) of 88 to 12. This polymer also had a number average molecular weight ratio of the polystyrene block in the high molecular weight portion (that produced by the first addition) to the low molecular weight portion (that produced by the second addition of styrene and monomer) of 3.5. As can be seen the flex life is better than doubled with the hardness being, if anything, slightly better.

Control run 5 utilizes an optimum weight ratio of styrene to diene (76/24) and what it is believed an optimum weight ratio of styrene addition in the first and second portions for conventional branched block polymers (53/23). As can be seen, this polymer exhibited better flex life than control 1 but at a substantial sacrifice in hardness. Control run 5 is to be compared with invention run 9 at the same amount of polymerized diene level which exhibited greatly increased flex life and increased hardness rather than decreased hardness as would normally be expected to be associated with better flex life. There is no apparent explanation as to why, with the same amount of polymerized diene, flex life can be improved and no deterioration in hardness and indeed, even an improvement in hardness.

It is to be noted that the polymerized styrene to diene weight ratio of the high molecular weight portion of the copolymer comes about as follows. Introduction of the first portion of styrene and initiator after polymerization produces a series of "living" polystyrene chains, each chain having a lithium atom on one end thereof which are relatively high in molecular weight. When the second initiator and styrene is added, new chains are formed each terminated with a lithium atom which do not grow to a length as great as those resulting from the first addition. Thus there is a mixture of long chains resulting from the first addition and short chains resulting from the second. By introduction of the diene, diene is added to the end of each of these chains adjacent to the lithium atom. Thus the column headed S/D Ratio High Molecular Weight Portion refers to the styrene to diene weight ratio in the chains resulting from the polymerization of the diene onto the ends of the polystyrene chains formed from the first addition of monomer. The column labeled "Polystyrene Block Ratio High/Low" simply refers to the ratio of the calculated number aver-

age molecular weight of the polystyrene blocks in the high molecular weight portion of chains formed by the first addition of initiator, to the calculated number average molecular weight of the polystyrene blocks in the chains formed by the second addition of initiator. It is to be noted that all of these values relate to the polymer chains prior to coupling to form the final product.

While this invention has been described in detail for purposes of illustration, it is not to be construed as lim-

ited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

I claim:

1. A coupled resinous block copolymer of a monovinyl-substituted aromatic compound and a conjugated diene, said copolymer having 71 to 81 weight percent polymerized monovinyl-substituted aromatic compound, wherein chains forming said copolymer prior to coupling comprise a high molecular weight portion and a low molecular weight portion, a ratio of calculated number average molecular weight of polymerized monovinyl-substituted aromatic compound blocks of said high molecular weight portion to polymerized monovinyl-substituted aromatic compound blocks of said low molecular weight portion being in the range of 3 to 7, said copolymer being produced by adding monovinyl-substituted aromatic compound monomer in first and second portions, a weight ratio of said monovinyl-substituted aromatic compound in said first portion to that in said second portion being within the range of 1:1.5 to 2:1, with 2.0 to 2.7 millimoles of initiator per mole of monomer in said first portion being introduced with said first portion and 3 to 5 millimoles of initiator per mole of monomer in said second portion being introduced with said second portion.

2. A composition according to claim 1 wherein said monovinyl-substituted aromatic compound is styrene and said conjugated diene is 1,4-butadiene, isoprene, or a mixture thereof.

3. A composition according to claim 2 wherein said ratio of calculated number average molecular weight of said polymerized monovinyl-substituted aromatic compound block of said high molecular weight portion to said calculated number average molecular weight of said polymerized monovinyl-substituted aromatic compound block of said low molecular weight portion is within the range of 3.5 to 4.8.

4. A composition according to claim 2 wherein the ratio of the calculated number average molecular weight of said polymerized monovinyl-substituted aromatic compound blocks in said high molecular weight portion plus polymerized diene blocks attached thereto to said polymerized monovinyl-substituted aromatic compound blocks of said low molecular weight portion plus polymerized diene attached thereto is within the range of 2 to 4.

5. A composition according to claim 2 wherein a ratio of said polymerized monovinyl-substituted aromatic compound blocks of said high molecular weight portion plus polymerized diene to said polymerized monovinyl-substituted aromatic compound blocks of said low molecular weight portion plus polymerized diene attached thereto based on number average molecular weight is within the range of 2.5 to 3.3.

6. A composition according to claim 5 wherein said styrene is present in an amount within the range of 75 to 77 weight percent based on the total weight of styrene plus diene.

7. A composition according to claim 6 wherein said styrene is present in an amount of about 76 weight percent.

8. A composition according to claim 7 wherein said composition has a shore D hardness of at least 73 and a flex life of at least 650 cycles.

9. A composition according to claim 2 wherein said copolymer has a styrene content of about 76 percent.

10. A method for preparing a polymer comprising

(a) introducing a first portion of monovinyl-substituted aromatic compound monomer into a reaction zone;

(b) introducing a first portion of an initiator into said reaction zone and polymerizing said first portion of said monovinyl-substituted aromatic compound;

(c) thereafter introducing a second portion of a monovinyl-substituted aromatic compound into said reaction zone, a weight ratio of said monovinyl-substituted aromatic compound in said first portion to monovinyl-substituted aromatic compound in said second portion being within the range of 1:1.5 to 2:1;

(d) introducing a second portion of said initiator into said reaction zone and polymerizing said second portion of said monovinyl-substituted aromatic compound, said first portion of initiator being introduced in an amount within the range of 2.0 to 2.7 millimoles per mole of said monomer in said first portion, and said second portion of initiator being introduced in an amount within the range of 3 to 5 millimoles per mole of said monomer in said second portion,

(e) introducing at least one conjugated diene into said reaction zone and polymerizing said at least one conjugated diene; and

(f) introducing a polyfunctional coupling agent into said reaction zone to form said polymer having a ratio of calculated number average molecular weight of polymerized monovinyl-substituted aromatic compound blocks from polymerizing said first portion of said monovinyl-substituted aromatic compound to that formed by polymerizing said second portion of said monovinyl-substituted aromatic compound within the range of 3 to 7.

11. A method according to claim 10 wherein said monovinyl-substituted aromatic compound is styrene and said conjugated diene is selected from 1,3-butadiene, isoprene, and mixtures thereof.

12. A method according to claim 11 wherein said wt ratio of monovinyl-substituted aromatic compound in said first and second portions is within the range of 1:1 to 1.9:1.

13. A method according to claim 12 wherein said styrene is present in an amount within the range of 75 to 77 weight percent based on the total weight of styrene and conjugated diene and wherein said diene is 1,3-butadiene.

14. A method according to claim 13 wherein said first portion of initiator is introduced in an amount within the range of 2.14 to 2.57 millimoles per mole of monomer and said second portion is introduced in an amount within the range of 3.66 to 4.93 millimoles per mole of monomer.

15. A method according to claim 14 wherein said coupling agent is epoxidized soybean oil containing about 4 epoxy groups per formula weight and said initiator is n-butyllithium.

* * * * *



US005436298A

United States Patent [19][11] **Patent Number:** **5,436,298****Moczygemba et al.**[45] **Date of Patent:** **Jul. 25, 1995**

[54] **BLOCK COPOLYMERS OF
MONOVINYLARENES AND CONJUGATED
DIENES AND PREPARATION THEREOF**

5,270,396 12/1993 Farrar, Jr. et al. 525/271
5,290,875 3/1994 Moczygemba et al. 525/314

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[21] **Appl. No.:** 308,240

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Related U.S. Application Data

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[52] **U.S. Cl.** 525/314; 525/89;
525/250; 525/271

[58] **Field of Search** 525/314, 271, 250, 89

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[57] ABSTRACT

A method for preparing resinous polymodal monovinylarene-conjugated diene block copolymers and polymers produced thereby are provided. The method comprises sequentially contacting under polymerization conditions:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a sequence of at least two charges selected from the group consisting of (i) initiator and a monovinylarene monomer, (ii) a mixture of monovinylarene monomer and conjugated diene monomer, (iii) a conjugated diene monomer, (iv) a monovinylarene monomer;
- (d) a coupling agent;

wherein the sequence of at least two charges in step (c) can be made in any order. In a preferred embodiment, at least three initiator charges are provided. In another preferred embodiment, at least three monovinylarene charges precede the first charge containing conjugated diene. In another preferred embodiment, at least four monovinylarene charges precede the first charge containing conjugated diene.

18 Claims, No Drawings

BLOCK COPOLYMERS OF MONOVINYLARENES AND CONJUGATED DIENES AND PREPARATION THEREOF

This is a continuation-in-part of application Ser. No. 8/130,039 filed Sep. 30, 1993, now abandoned.

FIELD OF THE INVENTION

This invention relates to block copolymers of 10 monovinylarenes and conjugated dienes and methods of preparation of these block copolymers.

BACKGROUND OF THE INVENTION

There has developed in the polymer field, and especially in the packaging and related industries, a need for thermoplastic polymers that can be formed into odorless, colorless, transparent articles having good impact strength and ductility. There are needs for polymers which are useful as single components as well as for use in blends with commonly used polymers to make articles with improved properties. The polymers satisfying these needs should be suitable for use with conventional extrusion, injection and blow molding equipment and also suitable for use in other methods of forming plastics into containers, tubes, films, fibers, and the like.

Much effort has been directed to the preparation of substantially transparent block copolymer resins with a variety of block structures produced by a variety of monomer addition sequences and a variety of coupling agents. Desirable properties and an economic advantage can be obtained by blending many monovinylarene-conjugated diene copolymers with polystyrene polymers. However, because blends of monovinylarene-conjugated diene copolymers with polystyrene polymers often contain unreacted styrene monomer, there is a need for high styrene content thermoplastic polymers which do not have undesirable unreacted styrene monomer while maintaining a good balance of physical and mechanical properties.

Odor caused by presence of unreacted styrene monomer in articles formed from various copolymers and blends of copolymers with polystyrene is a long-standing problem in applications where odorless, colorless materials which also have good impact strength and ductility are desirable. Specific examples include materials for water and food containers.

SUMMARY OF THE INVENTION

It is an object of this invention to provide novel resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes from which can be made transparent articles with an advantageous balance of properties including acceptable impact strength and ductility.

It is another object of this invention to provide novel resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes suitable for use as a replacement for blends of monovinylarene-conjugated diene copolymers with polymers of styrene. Further, it is an object to provide high styrene content resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes which can be used for applications requiring absence of unreacted styrene monomer and from which can be made articles having good impact strength and/or ductility and a good balance of other physical properties.

A further object of this invention is to provide novel processes for making resinous block monovinylarene-

conjugated diene copolymers, including copolymers suitable for use in the place of polymer blends.

We have discovered a method of preparing a block copolymer comprising sequentially contacting under polymerization conditions:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a sequence of at least two charges selected from the group consisting of
 - (i) initiator and a monovinylarene monomer;
 - (ii) a mixture of monovinylarene monomer and conjugated diene monomer;
 - (iii) a conjugated diene monomer; and
 - (iv) a monovinylarene monomer;

- (d) a coupling agent;

wherein said sequence of at least two charges in step (c) can be made in any order. In a preferred embodiment, at least three initiator charges are provided. In another preferred embodiment, at least three monovinylarene charges precede the first charge containing conjugated diene. In still another preferred embodiment, at least four monovinylarene charges precede the first charge containing conjugated diene.

The polymers of this invention are transparent, colorless resins from which can be made articles with a good balance of properties such as impact strength and/or ductility. Invention polymers with high styrene content can be used as replacements for blends of other monovinylarene-conjugated diene copolymers with polystyrene and have the advantage of having minimal amounts of unreacted styrene monomer.

DETAILED DESCRIPTION OF THE INVENTION

This is a continuation-in-part of application Ser. No. 08/130,039 filed Sep. 30, 1993 the disclosure of which is herein incorporated by reference.

We have discovered novel monovinylarene-conjugated diene block copolymers which can be used neat as a substitute for blends of other monovinylarene-conjugated diene copolymers with polystyrene to produce resins which can be formed into high styrene content articles with low unreacted styrene monomer content and advantageous impact properties and/or ductility.

The polymers of this invention are characterized as resinous non-rubbery block copolymers of at least one conjugated diene with at least one monovinylarene and are prepared so that, when the choice of coupling agent permits, at least a portion of the final product is of a branched, coupled character.

The polymers prepared according to this invention contain from about 55 to about 95, preferably from about 60 to about 95, more preferably from about 65 to about 95, weight percent copolymerized monovinylarene monomer based on the weight of total monomers employed. Correspondingly, the inventive copolymers contain from about 45 to about 5, preferably from about 40 to about 5, and more preferably from about 35 to about 5 weight percent copolymerized conjugated diene monomer based on the total weight of monomers in the copolymer.

Presently preferred when the invention copolymers are used as replacements for blends of other monovinylarene-conjugated diene copolymers with polystyrene, the polymers of this invention contain from about 80 to about 95, more preferably from 80 to 90 weight percent copolymerized monovinylarene

monomer based on the weight of total monomers employed. Correspondingly, the inventive copolymers contain from about 20 to about 5, more preferably from about 20 to about 10 weight percent copolymerized conjugated diene monomer based on the total weight of monomers in the copolymer.

Generally, the first monovinylarene monomer charge contains monovinylarene monomer in the amount in the range of from about 30 weight percent to about 50 weight percent based on the total weight of the final block copolymer.

Generally, the second monovinylarene monomer charge contains monovinylarene monomer in the amount in the range of from about 15 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

When employed, the third monovinylarene monomer charge typically contains monovinylarene monomer in the amount in the range of from about 5 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

Under certain circumstances, it is desirable to provide a fourth monovinylarene monomer charge. If a fourth monovinylarene monomer charge is employed, the third and fourth monovinylarene monomer charges each contain monovinylarene monomer in the range of from about 5 weight percent to about 20 weight percent based on the total weight of the final block copolymer.

More particularly, with reference to the Summary of the Invention, the following embodiments are provided comprising or consisting essentially of the following sequences. In one embodiment the sequence of charges is (c) is (i), (ii). In a second embodiment, the sequence of charges in (c) is (ii), (iv). In a third embodiment, the sequence of charges in (c) is (i), (iv), (iii). In a fourth embodiment, the sequence of charges in (c) is (i), (ii), (ii). In a fifth embodiment the sequence of charges in (c) is (ii), (i), (ii). In a sixth embodiment the sequence of charges in (c) is (i), (iii).

COMPONENTS

The process of this invention can be carried out using as an initiator any of the organomonoalkali metal compounds of the formula RM wherein R is an alkyl, cycloalkyl or arylcarbanion containing 4 to 8 carbon atoms and M is an alkyl metal cation. Mixtures of organoalkali metal compounds can be used. The presently preferred initiators are alkylmonolithium compounds, especially n-butyllithium or sec-butyllithium.

The conjugated diene monomers which can be used contain 4 to 6 carbon atoms and include 1,3-butadiene, 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene and mixtures thereof. Each of the charges containing conjugated diene in the same sequence of charges may be the same, but is not necessarily the same, conjugated diene monomer or mixture of conjugated diene monomers. The presently preferred conjugated diene monomer is 1,3-butadiene.

The monovinylarene monomers which can be used contain 8 to 12 carbon atoms and include styrene, alpha-methylstyrene, 4-methylstyrene, 3-methylstyrene, 2-methylstyrene, 4-ethylstyrene, 3-ethylstyrene, 2-ethylstyrene, 4-tert-butylstyrene, 2,4-dimethylstyrene and condensed aromatics such as vinyl naphthalene and mixtures thereof. Each of the charges containing monovinylarene monomer in the same sequence of charges may be the same, but is not necessarily the

same, monovinylarene monomer or mixture of monovinylarene monomers. The presently preferred monovinylarene monomer is styrene.

Examples of polar compounds which can be advantageously employed as randomizers and promoters are ethers, thioethers (sulfides) and tertiary amines. It is usually preferred to use ethers and sulfides in which the radicals attached to the oxygen or sulfur atoms are hydrocarbon radicals. It is to be understood also that mixtures of polar compounds can be employed in the practice of the present invention. Presently preferred are either tetrahydrofuran or diethyl ether.

Among the suitable coupling agents are the di- or multivinylarene compounds, di- or multiepoxides, di- or multiisocyanates, di- or multiimines, di- or multialdehydes, di- or multiketones, alkoxytin compounds, di- or multihalides, particularly silicon halides and halosilanes, mono-, di-, or multianhydrides, mono-, di-, or multiesters, preferably the esters of monoalcohols with polycarboxylic acids, diesters which are esters of monohydric alcohols with dicarboxylic acids, lactones, monobasic acids with polyalcohols such as glycerol, and the like, including compounds containing two or more of these groups and mixtures of two or more compounds.

Useful multifunctional coupling agents include epoxidized vegetable oils such as epoxidized soybean oil, epoxidized linseed oil and the like or mixtures thereof.

The presently preferred coupling agent is epoxidized vegetable oil. Presently preferred is epoxidized soybean oil.

PROCESS

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a first embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a second embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and a subsequent addition of a second charge of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, which is in turn followed by a charge of monovinylarene monomer, and a subsequent coupling step. Sheet made from such copolymer has a glossy hard surface and has excellent impact resistance.

The unique polymodal block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a third embodiment of this invention are produced by the unique sequence of three sequential charges of monovinylarene monomer and initiator, a subsequent addition of a charge of monovinylarene monomer, followed by a separate charge of a conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a fourth embodiment of this invention are produced by the unique sequence

of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by two separate sequential charges of a mixture of monovinylarene monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a fifth embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of a sequential charge of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, followed by a sequential charge of initiator and monovinylarene monomer, followed by a charge of a mixture of monovinyl monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a sixth embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by a separate charge of conjugated diene, and a subsequent coupling step.

In each of the embodiments of this invention the first initiator charge produces active living monovinylarene component polymer blocks with alkali metal atoms (from the initiator) on at least one end to form active reaction sites. The other ends of each of these polymeric chains will be end-capped with the "organo" portion of the organomonoalkali metal compound used as the initiator, i.e., the R portion of the RM compound. Each subsequent monomer charge adds monomer to the living polymer chain at the alkali metal reaction site. At each stage of charging, polymerization is usually allowed to continue until essentially no free monomer is present.

With each subsequent charge which includes initiator a new polymer-alkali metal species will be produced, and each subsequent monomer charge has an opportunity for polymerization of part of the charge with each of the existing polymer-alkali metal species. After virtually complete polymerization of the final monomer charge, the active living linear block copolymers are charged with a difunctional or polyfunctional coupling agent to below coupling of each of the living species with each of the other living species or with others of the same living species to form the desired polymodal block copolymers. If the coupling agent is not 100 percent efficient and/or if less or more than a stoichiometric amount of coupling agent is used, there can be some uncoupled terminated polymer chains of each of the species in the final reaction mixture.

Use of difunctional coupling agents will produce predominantly linear polymer chains. Depending upon amount and functionality, various degrees and kinds of branching may be accomplished with polyfunctional coupling agents.

The charging sequences of the various embodiments of this invention and the resulting polymers at each stage are exemplified using a selected monovinylarene monomer, conjugated diene and polyfunctional coupling agent in the following Tables 1-4. The "Organo" end caps are disregarded in designation of the terminal blocks because the end caps are so small in relation to

the polymer chains that they do not contribute to the properties of the resulting polymodal polymers.

TABLE 1

Invention Charging Sequence (First Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ —Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ —S ₂ —Li ₁ S ₂ —Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ —S ₂ —S ₃ —Li ₁ S ₂ —S ₃ —Li ₂ S ₃ —Li ₃
(d)	butadiene ₁ and styrene ₄	S ₁ —S ₂ —S ₃ —B ₁ /S ₄ Li ₁ S ₂ —S ₃ —B ₁ /S ₄ —Li ₂ S ₃ —B ₁ /S ₄ —Li ₃
(e)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where

S = styrene

B = butadiene

B/S = tapered block of conjugated diene and monovinylarene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 2

Invention Charging Sequence (Second Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ —Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ —S ₂ —Li ₁ S ₂ —Li ₂
(c)	butadiene ₁ and styrene ₃	S ₁ —S ₂ —B ₁ /S ₃ —Li ₁ S ₂ —B ₁ /S ₃ —Li ₂
(d)	styrene ₄	S ₁ —S ₂ —B ₁ /S ₃ —S ₄ —Li ₁ S ₂ —B ₁ /S ₃ —S ₄ —Li ₂
(e)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where

S = styrene

B = butadiene

B/S = tapered block of conjugated diene and monovinylarene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 3

Invention Charging Sequence (Third Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styron ₁	S ₁ —Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ —S ₂ —Li ₁ S ₂ —Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ —S ₂ —S ₃ —Li ₁ S ₂ —S ₃ —Li ₂ S ₃ —Li ₃
(d)	styrene ₄	S ₁ —S ₂ —S ₃ —S ₄ —Li ₁ S ₂ —S ₃ —S ₄ —Li ₂ S ₃ —S ₄ —Li ₃
(e)	butadiene ₁	S ₁ —S ₂ —S ₃ —S ₄ —B ₁ —Li ₁ S ₂ —S ₃ —S ₄ —B ₁ —Li ₂ S ₃ —S ₄ —B ₁ —Li ₃
(f)	coupling agent	polymodal block copolymers with styrene

TABLE 3-continued

Invention Charging Sequence (Third Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
		terminal blocks

where

S = styrene

B = butadiene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 4

Invention Charging Sequence (Fourth Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ -Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ -S ₂ -Li ₁ S ₂ -Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ -S ₂ -S ₃ -Li ₁ S ₂ -S ₃ -Li ₂ S ₃ -Li ₃
(d)	butadiene ₁ and styrene ₄	S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -Li ₁ S ₂ 13 S ₃ -B ₁ /S ₄ -Li ₂ S ₃ -B ₁ /S ₄ -Li ₃
(e)	butadiene ₂ and styrene ₅	S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₁ S ₂ -S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₂ S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₃
(f)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where

S = styrene

B = butadiene

B/S = tapered block of conjugated diene and monovinylarene

Li residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts = designation of the numerical order in which that particular component was charged or formed.

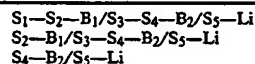
Fifth Embodiment Sequence;

- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,
- conjugated diene monomer/monovinylarene monomer mixture,
- initiator and monovinylarene monomer,
- conjugated diene monomer/monovinylarene monomer mixture,

and

- coupling agent.

Resulting Polymer Chains



where

S=styrene

B=butadiene

B/S=tapered block

Li=residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

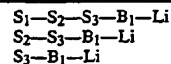
subscripts=designation of the numerical order in which that particular component was charged or formed.

Sixth Embodiment Sequence;

- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,

- conjugated diene monomer, and
- coupling agent.

Resulting Polymer Chains



where

S=styrene

B=butadiene

Li=residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts=designation of the numerical order in which that particular component was charged or formed.

In each of the embodiments the randomizer is usually added with the hydrocarbon diluent initially charged to the reactor. Each of the charges which has two monomers may be either a mixture of the two monomers or simultaneous charging of two separate monomers.

As can be seen from the intermediate products listed in the charging sequence tables above, in each of the embodiments of the invention there are at least two distinct species of polymer chains before coupling. The first and third through sixth embodiments have at least three distinct species of polymer chains before coupling. Thus, polymodal block copolymers comprising various proportions of relatively high, intermediate and low molecular weight species can be produced.

Tapered blocks in each of the growing polymer chains of embodiments having tapered blocks are produced by simultaneously charging with at least two monomers as shown in the preceding tables of the inventive charging sequences. The randomizer regulates tapering or random polymerization of the monovinylarene monomer and the conjugated diene in a mixed monomer charge. Choice of randomizer can be used to manipulate the degree and direction of taper in blocks resulting from charges of mixtures of monomers. The taper can be either a graduation from conjugated diene rich chain to monovinylarene rich chain or a graduation from a monovinylarene rich chain to conjugated diene rich chain according to preference of the initiator-randomizer complex for one type of monomer over the other.

The weight ratio of monovinylarene monomer to conjugated diene monomer in each of the tapered blocks is from about 1:0.63 to about 1:2, preferably from about 1:0.67 to about 1:1.8, and more preferably from about 1:0.8 to about 1:1.5. In the fourth embodiment, the weight ratios of monovinylarene monomer to conjugated diene monomer in each of the tapered blocks in the same polymer chain do not have to be the same.

The polymerization process is carried out in a hydrocarbon diluent at any suitable temperature in a range of about -10° to about 150° C., preferably in the range of about 0° to about 110° C., at pressures sufficient to maintain the reaction mixture substantially in the liquid phase. Charges of monomer and initiator are made in the presence of an amount of diluent or solvent sufficient to prevent excessive heat of reaction. Temperatures and pressures will peak during polymerization of each monomer charge and then decrease when essentially no free monomer is left to react. Appropriate hydrocarbon diluents include linear and cycloparaffins

such as butane, pentane, hexane, octane, cyclohexane, cyclopentane and mixtures thereof. Presently preferred is cyclohexane. Generally the choice of hydrocarbon or hydrocarbon mixture and the temperature is such that the resulting polymer is in solution.

Small amounts of polar compounds are used to improve the effectiveness of alkylmonoalkali metal initiators such as *n*-butyllithium; dissociation of the alkylmonoalkali metal initiators affects the rate of initiation and polymerization. The polar compounds also effect partial randomization of the vinylarene/conjugated diene so as to increase the random portion of the tapered block. The polar compounds are generally used in admixture with the hydrocarbon diluent.

The amounts of polar compounds used as randomizers and promoters of effectiveness of initiators in this invention will vary according to the reactivity and effectiveness of the particular randomizer used. The amounts of polar compounds used as randomizers will also vary according to the desired molecular structure of the portions of tapered blocks which result from conjugated diene addition. For example, when using tetrahydrofuran, and polymers with higher vinyl character resulting from 1,2 addition in excess of 1,4 addition are desired, larger amounts of tetrahydrofuran are used. However, use of too much randomizer can result in excessive polymer-lithium termination during polymerization and/or poor stability of the polymer and/or undesired side reactions, depending upon choice of randomizer. Use of too little randomizer would result in inefficient initiator use, compositional variations and broader molecular weight distribution.

The initial monovinylarene charge is made with the randomizer present for the additional effect of causing the monovinylarene component resulting from each initiator charge to be of relatively narrow molecular weight distribution. In each of the embodiments of this invention, by varying the amounts of initiator in each of the charges having initiator, the differences in molecular weights of the monovinylarene components resulting from each of these charges can be increased.

In each of the embodiments of the invention, amounts of initiator employed are those which will produce resins with desirable melt flow which can be used to make articles with a good balance of properties including minimal blueness, and good impact strength and/or ductility. Presently preferred when making invention polymers to be used as replacements for blends of other block copolymers with polystyrene are amounts of initiator in each of the initiator charges sufficient to obtain a block copolymer having a melt flow in the range from about 2 to about 50 g/10 minutes, more preferably from about 4 to about 30 g/10 minutes, and most preferably from about 7 to about 20 g/10 minutes, as determined by ASTM D1238-73, condition 200° C./5.0 kg. The amounts of initiator contemplated as useful in each of the charges having initiator are shown in Tables 5 through 8.

Use of too small an amount of initiator would result in high molecular weight polymers. Conversely, use of too large an amount of initiator would result in polymers having short chain polymeric species and low molecular weight.

Varying the weight ratios of amounts of each of the initiator charges made in each polymerization will result in variations of the proportionate amounts of species present in the copolymer. Other factors affecting the proportionate amounts of species present in the

copolymer include presence of impurities and/or scavengers in the reactor, effectiveness of the polar randomizer as a promoter and choice of coupling agent(s).

In any of the embodiments of this invention it is feasible to stretch out over an interval of time the addition of one or more of the increments of initiator, thus spreading (increasing) further the polymodality of the resulting product upon coupling.

The polymerization is carried out in a substantial absence of oxygen and water, preferably under an inert gas atmosphere. Prior to the coupling step, the reaction mass contains a very high percentage of molecules (polymer chains) in which an alkali metal cation is positioned at one end of each polymer chain. Impurities in the feed such as water or alcohol reduce the amounts of monoalkali metal polymer in the reaction mass.

After essentially complete polymerization of the final charge added to the polymer, one or more suitable difunctional or polyfunctional coupling agents is added. As used here, the term "coupling" means the bringing together and joining, by means of one or more central coupling atoms or coupling moieties, two or more of the living monoalkali metal-terminated polymer chains.

Any effective amount of the coupling agent can be employed. While the amount is not believed to be particularly critical, a stoichiometric amount relative to the active polymer-alkali metal tends to promote maximum coupling as a generality. Presently preferred is an amount of coupling agent slightly greater than stoichiometric relative to the active polymer-alkali metal. However, less than stoichiometric amounts can be used for higher degrees of coupling where desired for particular products of broadened molecular weight distribution.

Typically, in each of the embodiments of this invention, the total amount of coupling agent is in the range of about 0.005 to 10 phm (parts per 100 parts of total monomers employed in the polymerization). Preferred when most combinations of monomers and coupling agents are used to practice this invention is about 0.2 to about 0.6 phm of coupling agent, depending on amounts of initiator used. Presently most preferred is about 0.3 to about 0.5 phm, depending upon amounts of initiator used. Use of an insufficient amount of coupling agent will result in less complete coupling of the living polymer chains or, depending upon choice of coupling agent, more branching; use of an excessive amount of coupling agent will also result in more uncoupled chains.

At the conclusion of the coupling process, the coupled polymer may still contain bound polymeric alkali metal alkoxides depending on the type of coupling agent employed. The system is treated with an active compound such as water, alcohol, phenols, carbon dioxide or linear saturated aliphatic mono- and dicarboxylic acids to remove any remaining alkali metal from the copolymer chain.

Stabilization agents can be added to provide oxidative stability for the polymer during processing and handling and subsequent long term use by the customer. Commonly used stabilization processes can use a combination of compounds which include, but are not limited to, a hindered phenol and an organophosphite, particular examples of which are octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate and tris-nonylphenylphosphite.

After stabilization, the hydrocarbon diluent is then flashed from the polymer solution to increase the solids content. Flashing of the polymer cement may be fol-

lowed by desolventizing extrusion with vacuum in commercial production or by other vacuuming processes to achieve consistent solvent content of less than 0.3 weight percent.

The resinous copolymeric products can be, and normally are, compounded with anti-oxidants, anti-block-

ing agents, release agents and other additives, as known in the compounding arts.

Typical charging sequences and useful ranges of amounts of the charges for each of the first four embodiments of this invention are given in Tables 5 through 8. The amounts of initiator and randomizer indicated in the Table for each charge are also appropriate for the fifth and sixth embodiments.

TABLE 5

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (First Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(a)	randomizer ^c	0.001-3.0	0.01-1.0	0.02-0.5
	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	32-48	35-45	38-42
	monomer			
(b)	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	12-28	15-25	18-22
	monomer			
(c)	initiator	0.001-0.20	0.005-0.15	0.01-0.12
	and			
	monovinylarene	6-14	8-12	9-11
	monomer			
(d)	monovinylarene	5-25	10-20	13-17
	monomer and			
	conjugated diene	5-25	10-20	13-17
	monomer			
(e)	coupling agent	0.15-0.35	0.18-0.32	0.20-0.30

^aMonomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 6

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (Second Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(a)	randomizer ^c	0.001-3.0	0.01-1.0	0.02-0.5
	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	32-48	35-45	38-42
	monomer			
(b)	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	12-28	15-25	18-22
	monomer			
(c)	initiator	0.001-0.20	0.005-0.15	0.01-0.12
	and			
	monovinylarene	6-14	8-12	9-11
	monomer			
(d)	monovinylarene	6-14	8-12	9-11
	monomer and			
(e)	coupling agent	0.15-0.35	0.18-0.32	0.20-0.30

^aMonomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 7

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (Third Embodiment)				
Step	Component	Broad Range ^c	Preferred Range ^c	More Preferred Range ^c
(a)	randomizer ^c	0.001-3.0	0.01-1.0	0.02-0.5
	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	32-48	35-45	38-42
	monomer			
(b)	initiator	0.001-0.20	0.005-0.10	0.01-0.07
	and			
	monovinylarene	12-28	15-25	18-22
	monomer			
(c)	initiator	0.001-0.20	0.005-0.15	0.01-0.12

TABLE 7-continued

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (Third Embodiment)			
Step	Component	Broad Range ^c	Preferred Range ^c
	and monovinylarene monomer	6-14	8-12
(d)	monovinylarene monomer and conjugated diene monomer	5-25	10-20
		5-25	10-20
(e)	coupling agent	0.15-0.70	0.18-0.60
			0.20-0.50

^aMonomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 8

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (Fourth Embodiment)			
Step	Component	Broad Range ^b	Preferred Range ^b
(a)	randomizer ^c	0.001-3.0	0.01-1.0
	initiator	0.001-0.20	0.005-0.10
	and monovinylarene monomer	32-48	35-45
(b)	initiator	0.001-0.20	0.005-0.10
	and monovinylarene monomer	12-28	15-25
(c)	initiator	0.001-0.20	0.005-0.15
	and monovinylarene monomer	10-25	12-20
(d)	monovinylarene monomer and conjugated diene monomer	2-10	3-7
		2-10	3-7
(e)	monovinylarene monomer and conjugated diene monomer	3-12	5-9
		3-12	5-9
(f)	coupling agent	0.15-0.70	0.18-0.60
			0.20-0.50

^aMonomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

After coupling at least the coupled and uncoupled polymeric species shown in Tables 9 through 12 are present in the polymodal polymers of the first through fourth embodiments, respectively, of this invention.

TABLE 9

Polymeric Species Included in First Embodiment
S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃ -S ₂ -S ₁
S ₂ -S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃ -S ₂
S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃
S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃ -S ₂
S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃
S ₂ -S ₃ -B ₁ /S ₄ -x-S ₄ /B ₁ -S ₃
S ₁ -S ₂ -S ₃ -B ₁ /S ₄
S ₂ -S ₃ -B ₁ /S ₄
S ₃ -B ₁ /S ₄

S = monovinylarene block

B = conjugated diene block

B/S = tapered block of conjugated diene and monovinylarene

x = coupling moiety or coupling site

subscripts = indications of the charges which were the source of the polymer blocks.

TABLE 10

Polymeric Species Included in Second Embodiment
S ₁ -S ₂ -B ₁ /S ₃ -S ₄ -x-S ₄ -S ₃ /B ₁ -S ₂ -S ₁
S ₁ -S ₂ -B ₁ /S ₃ -S ₄ -x-S ₄ -S ₃ /B ₁ -S ₂

TABLE 10-continued

Polymeric Species Included in Second Embodiment
S ₂ -B ₁ /S ₃ -S ₄ -x-S ₄ -S ₃ /B ₁ -S ₂
S ₂ -B ₁ /S ₃ -S ₄
S ₁ -S ₂ -B ₁ /S ₃ -S ₄

S = monovinylarene block

B = conjugated diene block

B/S = tapered block of conjugated diene and monovinylarene

x = coupling moiety or coupling site
subscripts = indications of the charges which were the source of the polymer blocks.

TABLE 11

Polymeric Species Included in Third Embodiment
S ₁ -S ₂ -S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃ -S ₂ -S ₁
S ₂ -S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃ -S ₂
S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃
S ₁ -S ₂ -S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃ -S ₂
S ₁ -S ₂ -S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃
S ₂ -S ₃ -S ₄ -B ₁ -x-B ₁ -S ₄ -S ₃
S ₁ -S ₂ -S ₃ -S ₄ -B ₁
S ₂ -S ₃ -S ₄ -B ₁

TABLE 11-continued

Polymeric Species Included in Third Embodiment	
$S_3-S_4-B_1$	
S = monovinylarene block	
B = conjugated diene block	
x = coupling moiety or coupling site	
subscripts = indications of the charges which were the source of the polymer blocks.	

TABLE 12

Polymeric Species Included in Fourth Embodiment	
$S_1-S_2-S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3-S_2-S_1$	
$S_2-S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3-S_2$	
$S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3$	
$S_1-S_2-S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3-S_2$	
$S_1-S_2-S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3$	
$S_2-S_3-B_1/S_4-B_2/S_5-x-S_5/B_2-S_4/B_1-S_3$	
$S_1-S_2-S_3-B_1/S_4-B_2/S_5$	
$S_2-S_3-B_1/S_4-B_2/S_5$	
$S_3-B_1/S_4-B_2/S_5$	

S = monovinylarene block
 B = conjugated diene block
 B/S = tapered block of conjugated diene and monovinylarene
 x = coupling moiety or coupling site
 subscripts = indications of the charges which were the source of the polymer blocks.

In each of the embodiments, depending upon choice and amount of coupling agent or agents and whether coupling agents are charged as a mixture or incrementally, there can be present other polymeric species with varying degrees of branching.

BLENDS

The resinous polymodal copolymer products of this invention can be blended with other polymers such as polystyrene, acrylonitrile-butadiene-styrene copolymers (ABS), styrene-acrylonitrile copolymers (SAN), and other styrene copolymers. When less transparency is desired or transparency is not necessary, the invention copolymers can be blended with high impact polystyrene (HIPS) or polyolefins and/or olefin copolymers.

The compositions of this invention or blends thereof can be extruded, thermoformed, injection molded, blow molded, or made into films or sheets. The compositions of this invention can be used as high styrene content copolymer substitutes for blends of polystyrene with other monovinylarene-conjugated diene block copolymers in making articles with essentially no styrene monomer content. Non-inventive blends typically have 100-300 ppm residual styrene. Articles made from the compositions of this invention are transparent with low blueness, have good impact strength and have other physical properties within acceptable ranges for such applications as drinking cups, lids, bottles, other food containers, medical drainage units, shrink wrap and over-wrap.

TEST PROCEDURES

The blueness values (tristimulus value "b") were determined on a Model D 25 Hunter Lab Color Difference Meter using the Hunter Lab procedure. Blueness values are a measure of blue tint expressed as -b, where larger absolute numbers indicate more blueness. Generally, test specimens which exhibited -7.5 Hunter b blueness or less blueness were considered to have "low blueness". In each example, reported blueness (Hunter "b") values for injection molded test specimens are for the average of three readings on three stacked 0.050" by 2.5" diameter injection molded disks. Disks were injected

molded at 350° F./30 tons/2 minutes. Measurements were made against a black background.

Impact characterization of the extruded sheets was done using an Elmendorf Tearing Tester (Thwing-Albert Instrument Co.) in a manner similar to Spencer Impact Testing defined by ASTM D 3420. However, since the 4" sheet width was not sufficient to fill the entire sample clamp, the values were considered to be only relative. A $\frac{3}{8}$ " diameter tip was used with a 3200 g weight in place. The orientation of the sheet was such that the sheet machine direction was parallel to pendulum swing plane. The convex side of the sheet was up in all tests. Reported impact values are the average of five tests on the sheet and are considered, unitless because of the relative nature of results of the test procedure used.

Other properties were tested using ASTM procedures as shown in Table 13.

TABLE 13

Property	Test Procedures Used	
	ASTM Method	
Flow rate, g/10 min	D 1238-88	
Condition 200° C./5.0 kg		
Haze, %	D 1003-61 (1990)	
Transmittance, %	D 1003-61 (1990)	
Shore D hardness	D 2240-91	
Tensile strength at yield and break, MPa	D 638-91 at 50 mm/min Type I test specimens	
Elongation at yield and break, %	D 638-91 at 50 mm/min	
Flexural modulus, MPa	D 790-86	
Flexural strength, MPa	D 790-86	
Izod impact strength, notched, J/m	D 256-88	
Vicat softening point, °C.	D 1525-91	
Total energy dart drop, J	D 4272-85	

EXAMPLES

The following examples will describe in more detail the experimental process used and the polymodal block copolymers with vinylarene terminal blocks obtained as a result of invention processes. These examples should be taken as illustrative and not restrictive.

Styrene and butadiene were chosen as monomers to exemplify the invention, and randomizer, initiator, coupling agent and diluent appropriate for these monomers were used.

Example I

This example describes two invention polymerization runs (1, 2) which were made to exemplify the first embodiment of the invention. Polymerization was carried out in a stirred, 100-gallon carbon steel reactor with internal cooling coils. Sequential polymerizations were conducted under nitrogen employing essentially anhydrous reactants and conditions. Approximately 152 kg cyclohexane solvent (168.9 phm) were charged to the reactor. The tetrahydrofuran (THF) randomizer/promoter was in solution in the cyclohexane solvent initially charged to the reactor. The n-butyllithium initiator (from Lithium Corporation of America) was charged as a 2 weight percent solution in cyclohexane. The cyclohexane diluent containing the THF was preheated to about 40° C. before monomers were charged to the reactor. Monomers were styrene (from Sterling Chemical) and 1,3-butadiene (from Texas El Paso). Before charging, monomers were dried by passage over activated alumina (Kaiser A-201).

Reactants were charged to the reactor in the sequences and amounts indicated in Table 14. Lines were flushed with approximately 1.0 kg cyclohexane following each charge of monomer and with 0.5 Kg cyclohexane following each charge of initiator or additive. Polymerization was allowed to continue to completion after each monomer charge. Polymerization temperatures ranged from about 38° C. to about 110° C. and pressure ranged from about 2 psig to about 60 psig. Total monomer weight was about 90 kg.

After completion of the sequential polymerizations, Vikoflex® 7170, (a coupling agent comprising epoxidized soybean oil, available from Viking Chemical Company) was charged to the reactor. After completion of the coupling reaction, the reaction was terminated by adding 0.1 phm carbon dioxide and 0.2 phm water. The block copolymers were stabilized by adding a mixture containing 0.25 phm Irganox® 1076 (a hindered phenol commercially available from Ciba-Geigy) and 1.0 phm tris(nonylphenyl) phosphite (available as TNPP from GE Specialty Chemicals) to the reaction mixture. Each stabilizer was dissolved separately in cyclohexane and then the solutions were mixed together. Enough of the mixture was added to the reactor to provide 0.25 phm hindered phenol and 1 phm organic phosphite. In Runs 1 and 2 a microcrystalline wax (BE Square® 195) was also added as an antiblocking agent.

Substantially all of the remaining diluent was removed by passing the mixture through a Luwa Film-truder at 155° C., with a residence time of approximately 2 minutes. The resulting polymer was stranded and pelletized in a devolatilizing extruder at about 155° C. with a residence time of approximately 3-4 minutes.

TABLE 14

Invention Runs - First Embodiment		
	Run 1	Run 2
<u>Step 1</u>		
Cyclohexane, phm	168.9	168.9
Tetrahydrofuran, phm	0.04	0.3
n-Butyllithium initiator, phm	0.034	0.033
Styrene, phm	40	40
Cyclohexane, phm	1.7	1.7
Peak Polymerization Temperature, °C.	91.6	94.6
Peak Polymerization Pressure, psi	38.0	35.8
Polymerization Time, min	4	3
<u>Step 2</u>		
n-Butyllithium initiator, phm	0.030	0.022
Styrene, phm	20	20
Cyclohexane, phm	1.7	1.7
Peak Polymerization Temperature, °C.	89.8	90.1
Peak Polymerization Pressure, psi	36.4	37.0
Polymerization Time, min	4	3
<u>Step 3</u>		
n-Butyllithium initiator, phm	0.040	0.040
Styrene, phm	10	10
Cyclohexane, phm	1.7	1.7
Peak Polymerization Temperature, °C.	83.8	84.6
Peak Polymerization Pressure, psi	36.8	37.5
Polymerization Time, min	3	2
<u>Step 4</u>		
Butadiene, phm	15	15
Styrene, phm	15	15
Cyclohexane, phm	2.2	2.2

TABLE 14-continued

Invention Runs - First Embodiment		
	Run 1	Run 2
Peak Polymerization Temperature, °C.	111.0	111.5
Peak Polymerization Pressure, psi	55.8	54.7
Polymerization Time, min	8	6
Polymer Analysis (prior to coupling) (GPC area composition) ^a		
Peak 1	139.3	151.0
Peak 2	58.9	72.6
Peak 3	37.0	44.6
<u>Step 5 (Coupling)</u>		
Vikoflex 7170, phm	0.27	0.25
Cyclohexane, phm	0.6	0.6
Temperature, °C.	99.3	98.4
Pressure, psi	50	50.5
<u>Step 6 (Terminating)</u>		
Water, phm	0.20	0.2
Carbon Dioxide, phm	0.17	0.17
<u>Step 7 (Stabilizing)</u>		
Stabilizer Mixture, phm	1.25	1.25
Antiblocking agent, phm	.18	.18
<u>Recovered Resin</u>		
Melt Flow, g/10 min	8.0	8.6

^aResponse of a dielectric detector in an Applied Automation process control GPC.

Injection molded test specimens of the block copolymers exhibited the properties shown in Table 15.

TABLE 15

Physical Properties of Injection Molded Articles (First Embodiment)		
Property	Invention Polymer 1	Invention Polymer 2
Melt flow, g/10 min	8.0	8.6
Haze, %	0.9	0.9
Hunter blueness, b	-2.42	-4.28
Shore D Hardness	77	75
Notched Izod impact, J/m	22.4	24.0
<u>Tensile strength</u>		
yield, MPa	44.7	42.3
break, MPa	28.0	28.6
<u>Elongation</u>		
yield, %	5.42	5.09
break, %	89.8	68.3
Flexural modulus, MPa	1765	1724

Example II

This example describes four invention polymerization runs which were made to exemplify the second embodiment of the invention. Styrene (from Sterling Chemical) and 1,3-butadiene (from Texas El Paso) were dried by passage over activated alumina (Kaiser A-201), and then copolymerized and coupled in a 4-stage process using n-butyllithium initiator (from Lithium Corporation of America).

Polymerization runs were carried out under nitrogen in a stirred, jacketed, stainless steel 7.6-liter reactor employing essentially anhydrous reactants and conditions. The anhydrous mixtures were stirred continuously during the polymerization process. The cyclohexane diluent, which contained 0.04 phm tetrahydrofuran (THF) in each polymerization in this example, was preheated to about 50° C. before monomers were charged to the reactor. The n-butyllithium was charged as a 2 weight percent solution in cyclohexane. In the polymerization step in which both butadiene and sty-

rene were charged, they were charged simultaneously as a mixture.

In the coupling step, the Vikoflex® 7170 coupling agent used was an epoxidized vegetable oil commercially available from Viking Chemical Company. In the terminating step, carbon dioxide from a pressurized container was admitted to provide about 0.4 phm carbon dioxide to the reactor. Water was also added in an amount slightly in stoichiometric excess of the initiator to separate the lithium residues from the polymer chains.

The antioxidant mixture added in the stabilizing step contained a hindered phenol [octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate, commercially available as Irganox® 1076 from Ciba-Geigy] and an organic phosphite (trisnonylphenyl phosphite, available as TNPP from GE Specialty Chemicals). Each stabilizer was dissolved separately in cyclohexane and mixed together. Enough of the mixture was added to the reactor to provide 0.25 phm hindered phenol and 1 phm organic phosphite. In all four runs, a microcrystalline wax (BE Square® 195) was also added as an antiblocking agent.

After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3–20 phm cyclohexane solvent and cleared with a nitrogen purge.

Following the stabilization step, each copolymer solution was flashed at 178°–180° C. to remove a portion of the diluent. Substantially all of the remaining diluent was removed in a vacuum oven by drying at 90° C. for one hour. The resulting polymer was chopped in a granulator into crumb and then dried for an additional hour in a vacuum oven.

In each of the four runs (3, 4, 5 and 6), 1500 g total monomers (butadiene and styrene) were used. About 76 weight percent of the total amount of cyclohexane diluent (3130 g) was charged initially. The remaining cyclohexane diluent was added during the run as a diluent or flush for the various reactants added in subsequent steps. In these four polymerizations, the weight ratio of total monomers charged was 85:15 styrene/butadiene.

The charges and the results of the runs are summarized in Table 16. Tapered butadiene/styrene blocks were formed in step 3 by charging both butadiene and styrene monomers. The charging sequence used was i, S₁, i, S₂, B₁/S₃, S₄, coupling agent. The monomer ratios corresponding to the S₁, S₂, B₁/S₃, S₄, sequence were 40, 20, 15/15, 10. Weight ratios of amounts of initiator used in the first two steps of each of the five runs was kept constant at 1:1.

The devolatilized copolymers from runs 3, 4, 5 and 6 were designated invention copolymers 3, 4, 5 and 6 had melt flows of 5.0 g/10 min, 9.4 g/10 min, 9.4 g/19 min and 7.4 g/10 min, respectively. The differences in melt flows were attributable to differences in amounts of initiator used in each of the four runs.

Injection molded test specimens of the block copolymers exhibited the properties shown in Table 18 after Example III.

TABLE 16

Invention Runs - Second Embodiment				
	Run 3	Run 4	Run 5	Run 6
<u>Step 1</u>				
Cyclohexane, phm	157	157	157	157
Tetrahydrofuran, phm	0.04	0.30	0.50	1.0
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.03
Cyclohexane, phm	4.6	4.6	4.6	4.6

TABLE 16-continued

Invention Runs - Second Embodiment				
	Run 3	Run 4	Run 5	Run 6
Styrene, phm	40	40	40	40
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	80.5	89.4	92.1	83.6
Peak Polymerization Pressure, psi	22	29	35	28
Polymerization Time, min	12	12	12	12
<u>Step 2</u>				
n-Butyllithium initiator, phm	0.06	0.055	0.05	0.04
Cyclohexane, phm	4.6	4.6	4.6	4.6
Styrene, phm	20	20	20	20
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	81.3	84.8	88.3	86.7
Peak Polymerization Pressure, psi	30	34	28	37
Polymerization Time, min	11	11	11	11
<u>Step 3</u>				
Styrene, phm	15	15	15	15
Butadiene, phm	15	15	15	15
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	107.2	109.9	115.4	114.5
Peak Polymerization Pressure, psi	64	41	47	62
Polymerization Time, min	18	16	16	16
<u>Step 4</u>				
Styrene, phm	10	10	10	10
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	87.9	89.8	93.3	93.3
Peak Polymerization Pressure, psi	68	68	37	71
Polymerization Time, min	12	12	12	12
<u>Step 5 (Coupling)</u>				
Vikoflex® 7170, phm	0.24	0.22	0.20	0.18
Cyclohexane, phm	4.6	4.6	4.6	4.6
Temperature, °C.	90	92	86	95
Pressure, psi	87	96	63	97
<u>Step 6 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4	0.4
Temperature, °C.	98	100	107	121
Pressure, psi	82	57	70	86
<u>Step 7 (Stabilizing)</u>				
Stabilizer Mixture, phm	1.25	1.25	1.25	1.25
Antiblocking agent, phm	0.3	0.3	0.3	0.3
<u>Recovered Resin</u>				
Melt Flow, g/10 min	5.0	9.4	9.4	7.4

Example III

Two more polymerization runs (7 and 8) were carried out according to the second embodiment of the invention to demonstrate the use of larger volumes of monomers. The procedure of Example I was followed with the exception that the sequence of charges shown in Table 17 was used. Again, the weight ratio of styrene to butadiene charged was 85 to 15. Samples were made with i, S₁, i, S₂, B₁/S₃, S₄ addition sequence followed by coupling; monomer ratios of 35, 20, 15/15, 15 were used.

In this example, 0.032 phm (run 7) initiator and 0.031 phm initiator (run 8) was charged in the first steps of the two runs. The amount of initiator charged in the second step was 0.075 phm (run 7) and 0.064 phm (run 8) for a range of ratios of amount of initiator in first step to amount in second step of 1:2.3 (run 7) to 1:2.1 (run 8).

Copolymers from runs 7 and 8, were devolatilized to form invention copolymers 7 and 8, which had melt flows of 8.1 g/10 min and 8.2 g/10 min, respectively. Injection molded test specimens of invention copoly-

mers 7 and 8 exhibited the properties shown in Table 18.

TABLE 17

Invention Runs - Second Embodiment		
Components ^a	Run 7	Run 8
<u>Step 1</u>		
Cyclohexane, phm	168.9	168.9
Tetrahydrofuran	0.04	0.3
n-Butyllithium		
initiator, phm	0.032	0.031
Styrene, phm	35	35
Polymerization Time, min	4	2
Peak Polymerization	84.9	89.6
Temperature, °C.		
Peak Polymerization	35.1	36.4
Pressure, psi		
<u>Step 2</u>		
n-Butyllithium	0.075	0.064
initiator, phm		
Styrene, phm	20	20
Polymerization Time, min	3	3
Peak Polymerization	86.8	86.7
Temperature, °C.		
<u>Step 3</u>		
Butadiene, phm	15	15
Styrene, phm	15	15
Polymerization Time, min	8	6
Peak Polymerization	105.2	107.8
Temperature, °C.		
<u>Step 4</u>		
Styrene, phm	15	15
Polymerization Time, min	3	3
Peak Polymerization	88.0	88.9
Temperature, °C.		
<u>Step 5 (Coupling)</u>		
Vikoflex 7170, phm	0.28	0.25
Temperature, °C.	77.4	74.5
<u>Step 6 (Terminating)</u>		
Water, phm	0.2	0.2
Carbon Dioxide, phm	0.17	0.17
<u>Step 7 (Stabilizing)</u>		
Stabilizer Mixture, phm	1.25	1.25
BE Square wax	0.18	0.18
<u>Recovered Resin</u>		
Melt Flow, g/10 min	8.1	8.2

^aAfter each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5-20 phm cyclohexane diluent and cleared with nitrogen.

TABLE 18

Physical Properties of Injection Molded Articles Made from Invention Polymers (Second Embodiment)						
Property	Invention Polymer 3	Invention Polymer 4	Invention Polymer 5	Invention Polymer 6	Invention Polymer 7	Invention Polymer 8
Melt flow, g/10 min	5.0	9.4	9.4	7.4	8.1	8.2
Haze, %	1.0	0.7	1.1	1.4	1.0	0.9
Hunter	-1.6	-3.1	-2.3	-2.1	-1.45	-1.63
blueness, b						
Shore D Hardness	77	77	76	75	78	78
Notched Izod	20.3	21.9	21.9	21.9	24.6	23.0
impact, J/m						
<u>Tensile strength</u>						
yield, MPa	43.4	39.1	38.5	33.5	39.0	37.5
break, MPa	30.3	24.1	24.9	22.9	26.4	25.9
<u>Elongation</u>						
yield, %	5.95	6.21	5.73	5.47	4.8	5.01
break, %	163	116	96	116	76.5	98.7
Flexural	1565	1393	1407	1241	1662	1565
modulus, MPa						

Example IV

A polymerization was made to demonstrate the third 65 embodiment of the invention. This run (9) was carried out according to the procedure of Example I with the exception that the sequences and amounts of charges

shown in Table 19 were used. The weight ratio of styrene to butadiene charged was 85 to 15.

The coupled devolatilized copolymers from run 9 contained no tapered blocks, contained a single internal butadiene block (disregarding any coupling moiety) and bad terminal styrene blocks on each of the extending arms of each of the coupled polymeric species.

A copolymer from run 9 was devolatilized to form invention copolymer 9 which had a melt flow of 10.2 g/10 min.

TABLE 19

Invention Runs - Third Embodiment	
	Run 9
<u>Step 1</u>	
Cyclohexane, phm	168.9
Tetrahydrofuran, phm	0.04
n-Butyllithium	0.032
initiator, phm	
Styrene, phm	40
Cyclohexane, phm	1.7
Peak Polymerization	90.0
Temperature, °C.	
Peak Polymerization	36.7
Pressure, psi	
Polymerization Time, min	5
<u>Step 2</u>	
n-Butyllithium	0.034
initiator, phm	
Styrene, phm	20
Cyclohexane, phm	1.7
Peak Polymerization	87.7
Temperature, °C.	
Peak Polymerization	34.4
Pressure, psi	
Polymerization Time, min	4
<u>Step 3</u>	
n-Butyllithium initiator, phm	0.100
Styrene, phm	10
Cyclohexane, phm	1.7
Peak Polymerization	85.1
Temperature, °C.	
Peak Polymerization	36.7
Pressure, psi	
Polymerization Time, min	3
<u>Step 4</u>	
Styrene, phm	15
Cyclohexane, phm	1.1
Peak Polymerization	87.3

Temperature, °C.
Peak Polymerization 40.0
Pressure, psi
Polymerization time, min 3
Step 5
Butadiene, phm 0.5

TABLE 19-continued

Invention Runs - Third Embodiment	
	Run 9
Cyclohexane, phm	1.1
Peak Polymerization Temperature, °C.	105.2
Peak Polymerization Pressure, psi	51.4
Polymerization Time, min	5
Polymer Analysis (prior to coupling) (GPC area composition) ^a	
Peak 1	123.6
Peak 2	43.4
Peak 3	22.9
Step 6 (Coupling)	
Vikoflex 7170, phm	0.43
Cyclohexane, phm	0.6
Temperature, °C.	97.2
Pressure, psi	49.6
Step 7 (Terminating)	
Water, phm	0.2
Carbon Dioxide, phm	0.17
Temperature, °C.	—
Pressure, psi	—
Step 8 (Stabilizing)	
Stabilizer Mixture, phm	1.25
Antiblocking agent, phm	0.18
Recovered Resin	
Melt Flow, g/10 min	10.2

^aResponse of a dielectric detector in an Applied Automation process control GPC.

Injection molded test specimens of the polymodal block copolymer of run 9 were made and found to exhibit the properties shown in Table 20.

TABLE 20

Physical Properties of Injection Molded Articles (Third Embodiment)	
Property	Invention Polymer 9
Melt flow, g/10 min	10.2
Haze, %	0.7
Hunter blueness, b	-1.75
Shore D Hardness	77
Notched Izod impact, J/m	24.0
Tensile strength	
yield, MPa	47.9
break, MPa	48.3
Elongation	
yield, %	5.33
break, %	5.63
Flexural modulus, MPa	1972

Example V

A polymerization run was made for the purpose of demonstrating the fourth embodiment of this invention. The method of Example I was used, with the exception that the sequence and amounts of charges shown in Table 21 were used.

The polymodal block copolymer of run 10 (designated invention copolymer 10) had two sequentially internal tapered blocks and terminal styrene blocks on each of the coupled polymeric species. The block copolymer had a styrene to butadiene ratio of 88 to 12 and a melt flow of 20.0 g/10 min.

Injection molded test specimens of invention copolymer 10 exhibited the properties shown in Table 22.

TABLE 21

Invention Run - Fourth Embodiment	
	Run 10
Step 1	
Cyclohexene, phm	168.9
Tetrahydrofuran, phm	0.04
n-Butyllithium initiator, phm	0.022
Styrene, phm	40
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	84.0
Peak Polymerization Pressure, psi	34.6
Polymerization Time, min	5
Step 2	
n-Butyllithium initiator, phm	0.020
Styrene, phm	20
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	86.5
Peak Polymerization Pressure, psi	83.9
Polymerization Time, min	3
Step 3	
n-Butyllithium initiator, phm	0.100
Styrene, phm	16
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	87.2
Peak Polymerization Pressure, psi	37.1
Polymerization Time, min	3
Step 4	
Butadiene, phm	5
Styrene, phm	5
Cyclohexane, phm	2.2
Peak Polymerization Temperature, °C.	81.2
Peak Polymerization Pressure, psi	38.1
Polymerization Time, min	9
Step 5	
Butadiene, phm	7
Styrene, phm	7
Cyclohexane, phm	2.2
Peak Polymerization Temperature, °C.	87.3
Peak Polymerization Pressure, psi	43.8
Polymerization Time, min	7
Polymer Analysis (prior to coupling) (GPC area composition) ^a	
Peak 1	187.3
Peak 2	36.1
Step 6 (Coupling)	
Vikoflex 7170, phm	0.41
Cyclohexane, phm	0.6
Temperature, °C.	74.5
Pressure, psi	41.7
Step 7 (Terminating)	
Water, phm	0.2
Carbon Dioxide, phm	0.17
Temperature, °C.	—
Pressure, psi	—
Step 8 (Stabilizing)	
Stabilizer Mixture, phm	1.25
Antiblocking agent, phm	0.18
Recovered Resin	
Melt Flow, g/10 min	20.0

^aResponse of a dielectric detector in an Applied Automation process control GPC.

TABLE 22

Physical Properties of Injection Molded Articles (Fourth Embodiment)	
Property	Invention Polymer 10
Melt flow, g/10 min	20.0
Haze, %	0.8
Hunter blueness, b	-1.7
Shore D Hardness	80
Notched Izod impact, J/m	20.8
<u>Tensile strength</u>	
yield, MPa	50.4
break, MPa	31.5
<u>Elongation</u>	
yield, %	6.37
break, %	15.71
Flexural modulus, MPa	1800

Example VI

Three more polymers were prepared to use in blends for comparison with the invention polymers. Polymerization runs 11, 12 and 13 were carried out according to the method of Example II, except that the weight ratio of styrene to butadiene charged was 75 to 25 and samples were made with i, S₁, i, S₂, B₁/S₃ addition sequence followed by coupling; monomer ratios of 40, 10, 25/25 were used. The charges and results of the runs are shown in Table 23.

In each of the three runs of this example, 0.03 phm initiator was charged in the first step. The amount of initiator charged in the second step was varied from 0.08 phm (run 11) to 0.095 phm (run 13) for a range of ratios of amount of initiator in first step to amount in second step from 1:2.7 (run 11) to 1:3.2 (run 13).

Copolymers from runs 11, 12 and 13 were devolatilized to form comparative copolymers 11, 12 and 13, which had melt flows of 5.0 g/10 min, 5.4 g/10 min, and 7.1 g/10 min, respectively.

TABLE 23

Components ^a	Comparative Runs		
	Run 11	Run 12	Run 13
<u>Step 1</u>			
Cyclohexane, phm	145	145	145
Tetrahydrofuran	0.04	0.04	0.04
n-Butyllithium	0.03	0.03	0.03
initiator, phm			
Styrene, phm	40	40	40
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	77	79	76
<u>Step 2</u>			
n-Butyllithium	0.08	0.085	0.095
initiator, phm			
Styrene, phm	10	10	10
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	64	71	65
<u>Step 3</u>			
Butadiene, phm	25	25	25
Styrene, phm	25	25	25
Polymerization Time, min	16	16	16
Peak Polymerization Temperature, °C.	117	121	111
<u>Step 4 (Coupling)</u>			
Vikoflex 7170, phm	0.4	0.4	0.4
Time, min	16	16	16
Temperature, °C.	88	87	89
<u>Step 5 (Terminating)</u>			
Water, phm	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4
Time, min	25	25	25
Temperature, °C.	82	82	84

TABLE 23-continued

Components ^a	Comparative Runs		
	Run 11	Run 12	Run 13
<u>Step 6 (Stabilizing)</u>			
Stabilizer Mixture, phm	1.25	1.25	1.25
BE Square wax	0.15	0.15	0.15
Time, min	5	5	5
<u>Recovered Resin</u>			
Melt Flow, g/10 min	5.0	5.4	7.1
Mw/Mn, thousands	181/114	177/111	138/93
Heterogeneity Index	1.6	1.6	1.69

^aAfter each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5-20 phm cyclohexane diluent and cleared with nitrogen.

Example VII

Two more comparative polymers (14 and 15) were used for making comparisons of physical properties of blends of the comparative polymers with polystyrene to physical properties of the invention copolymers.

Comparative polymer 14 was a resinous styrene-butadiene copolymer with a melt flow of 8.4 g/10 min. Polymer 14 was polymodal from multiple initiator and monomer charges (S, i, i, S, B, i, S, B) and coupled with an epoxidized vegetable oil coupling agent. Polymer 14 contained nominally 75 wt % styrene and 25 wt % butadiene with no styrene/butadiene tapered blocks. Comparative polymer 14 is similar to the third embodiment of the invention with the exceptions that comparative polymer 14 had a charge of butadiene in place of the third charge of initiator and monovinylarene monomer in the third embodiment and the third embodiment can have a proportionately higher monovinylarene content relative to conjugated diene content than comparative polymer 14 had. Polymer 14 formed 50:50 by weight blends with polystyrene that had high blueness and modest physical properties.

Comparative polymer 15 was a styrene-butadiene copolymer with no tapered block segments. Polymer 15 contained nominally 75 wt % styrene and 25 wt % butadiene and had a melt flow of 8.8 g/10 min. It had a polymodal molecular weight from multiple initiator and monomer charges (S, i, i, S, B) and was coupled with an epoxidized vegetable oil coupling agent. Comparative polymer 15 was similar to the third embodiment with the exceptions that: the third embodiment was made with two additional charges next preceding the conjugated diene charge, i.e., a charge of monovinylarene monomer and initiator followed by a charge of monovinylarene monomer; and, the third embodiment can contain a proportionately much larger monovinylarene content than that of comparative polymer 15. Polymer 15 formed 50:50 blends by weight with polystyrene that had low blueness and modest impact properties.

Example VIII

A series of blends of the comparison polymers from Examples VI and VII was prepared with Novacor® 555 general purpose polystyrene to demonstrate the properties of blends of the comparative copolymers containing total amounts of styrene similar to the total amounts of monovinylarene content in the invention copolymers of Examples I-V.

The blends were 50:50 or 60:40 styrene:butadiene by weight as indicated in the table and were prepared by solution blending in cyclohexane in a reactor at 100° C. with stirring for one hour. Each solution was flashed to

remove the solvent and the polymer was dried, chopped in a granulator, and dried again. The dry polymer was processed on a roll mill and chopped again before injection molding on an Arburg model 90 injection molder with zones 1, 2, 3, and nozzle at 210° C., 210° C., 220° C., and 210° C., respectively, to make specimens to test for properties.

For convenient reference, blends are designated with the corresponding polymer numbers. For example, a blend prepared from comparative polymer 11 and polystyrene is comparative blend 11.

The results of tests of articles made from the comparative blends are shown in Table 24. Test specimens made from the blends of comparative polymers 11-15 exhibit significantly higher haze and blueness and significantly lower notched izod impact strengths than those of the inventive polymers. Thus the inventive polymers are superior to the blends in these areas for most applications. Also, the inventive polymers from embodiments 1 and 2 exhibit significantly higher tensile elongation at break than do the blend polymers, indicating greater ductility. Generally, the other properties of the blends and inventive polymers are similar.

TABLE 24

Property	Physical Properties of Test Specimens Made from Blends of Comparison Polymers with Polystyrene				
	Comparative Blend 11	Comparative Blend 12	Comparative Blend 13	Comparative Blend 14	Comparative Blend 15
Blend ratio, S-B:PS ^a	50:50	50:50	50:50	50:50	50:50
Blend melt flow, g/10 min	30.2	10.7	12.8	16.8	17.5
Haze, %	8.1	3.4	4.2	4.3	2.7
Hunter blueness, b	-16.2	-16.9	-17.1	-20.3	-16.8
Shore D Hardness	77	77	77	77	79
Notched Izod impact, J/m	14.6	17.1	12.3	12.4	13.9
Vicat, °C	82.9	92.1	92.0	85.3	89.3
<u>Tensile strength</u>					
yield, MPa	40.2	44.5	42.5	37.8	42.6
break, MPa	27.5	33.7	21.4	28.0	33.4
<u>Elongation</u>					
yield, %	5.3	6.2	6.2	4.8	4.8
break, %	18.2	14.7	13.7	32.0	15.77
Flexural modulus, MPa	1836	2091	2016	1979	2124

S-B:PS = Styrene-butadiene copolymer:polystyrene

Example IX

To provide comparison polymers having more than one tapered block, three more polymerization runs (16, 17 and 18) were carried out according to the procedures described in Example II, with the exception that the sequences and amounts of charges were as shown in Table 25. Tapered butadiene/styrene blocks were formed in the third and fourth steps by charging a mixture of butadiene and styrene monomers. The monomer addition sequence was i, S₁, i, S₂, B₁/S₃, B₂/S₄ followed by coupling; the monomer weight ratios were 40, 10, 12.5/12.5, 12.5/12.5, respectively. The polymers were 75 percent styrene and 25 percent butadiene.

In each of the three runs of this example the weight ratio of amount of initiator in the first step to the amount in the second step was kept constant at 1:1 with the absolute amount varied from 0.06 phm (run 16) to 0.055 phm (run 18).

The copolymers produced in the three runs were designated comparative copolymers 16, 17, and 18, and had melt flows of 14.3, 6.40 and 10.8 respectively. It is believed that lower melt flows are attributable to lower

amounts of initiator. The polymerizations of invention runs 16, 17 and 18 are shown in Table 25.

TABLE 25

Components ^a	Comparative Runs		
	Run 16	Run 17	Run 18
<u>Step 1</u>			
Cyclohexane, phm	145	145	145
Tetrahydrofuran, phm	0.04	0.04	0.04
n-Butyllithium initiator, phm	0.06	0.05	0.055
Styrene, phm	40	40	40
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	85	82	84
<u>Step 2</u>			
n-Butyllithium initiator, phm	0.06	0.05	0.055
Styrene, phm	10	10	10
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	69	69	70
<u>Step 3</u>			
Butadiene, phm	12.5	12.5	12.5
Styrene, phm	12.5	12.5	12.5
Polymerization Time, min	16	16	16
Peak Polymerization Temperature, °C.	84	83	84
<u>Step 4</u>			
Butadiene, phm	12.5	12.5	12.5
Styrene, phm	12.5	12.5	12.5
Polymerization Time, min	16	16	16
Peak Polymerization Temperature, °C.	96	102	102
<u>Step 5 (Coupling)</u>			
Vikoflex 7170, phm	0.4	0.4	0.4
Time, min	16	16	16
Temperature, °C.	82	89	89
<u>Step 6 (Terminating)</u>			
Water, phm	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4
Time, min	25	25	25
Temperature, °C.	80	82	82
<u>Step 7 (Stabilizing)</u>			
Stabilizer Mixture, phm	1.25	1.25	1.25
Antiblocking agent, phm	0.15	0.15	0.15
Time, min	5	5	5
Temperature, °C.	80	n.a.	81
<u>Recovered Resin</u>			
Melt Flow, g/10 min	14.3	6.4	10.8
Mw/Mn, thousands	154/104	173/115	147/91

TABLE 25-continued

Components ^a	Comparative Runs		
	Run 16	Run 17	Run 18
Heterogeneity Index	1.48	1.50	1.62

^aAfter each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5-20 phm cyclohexane diluent and cleared with nitrogen.

Example X

A series of blends of double tapered block comparative polymers with polystyrene was prepared for comparison of the properties of articles made from the blends to properties of invention polymers having two tapered blocks and similar total styrene content. Copolymers 16, 17, and 18 from Example IX were blended as described in Example VIII in 50:50 by weight mixtures with general purpose polystyrene to form comparative blends 16, 17, and 18. Test specimens were injection molded from the blends as described in Example VIII.

The results (Table 26) show that articles made from blends of comparative polymers 16, 17, and 18 had more modest Izod impact values than those made from invention polymer 10 which also had two tapered blocks (shown in Table 22). Articles made from blends of the invention polymers also have less blueness than those made from comparative blends 16, 17 and 18.

TABLE 26

Physical Properties of Comparative Polymer Blends with Polystyrene ^a				
Property	Comparative Blend 16	Comparative Blend 17	Comparative Blend 18	Comparative Blend 14
Blend melt flow, g/10 min	14.8	12.0	14.8	16.8
Haze, %	4.1	4.0	5.1	4.3
Hunter blueness, b	-17.9	-18.5	-17.9	-20.3
Shore D hardness	76	77	76	77
Notched Izod impact, J/m	14.9	17.1	19.2	12.3
Vicat softening, °C.	89.3	90.9	90.5	85.3
<u>Tensile Strength</u>				
yield MPa	43.2	43.9	42.5	37.8
break MPa	29.6	28.7	28.7	28.0
<u>Elongation</u>				
yield, %	6.4	6.5	6.5	4.8
break, %	17.9	16.7	13.6	32.0
Flexural modulus, MPa	1988	1949	1986	1979

^a50:50 Styrene-butadiene copolymer:polystyrene

Example XI

Polymerization runs were carried out in a stirred, 100 gallon carbon steel reactor with internal cooling coils employing essentially anhydrous reactants and conditions.

Sequential polymerizations were conducted under nitrogen. Approximately 158 kg cyclohexane solvent (175 phm) were charged to the reactor. Reactants were charged to the reactor in the sequence and amount indicated in Table 27. Lines were flushed with 0.5 kg cyclohexane following each charge. Polymerization was allowed to continue to completion after each monomer or monomer mixture charge. Polymerization temperatures ranged from about 38° C. to about 110° C. and pressure ranged from about 2 psig to about 60 psig. Total monomer weight was about 90 kg.

After completion of sequential polymerizations, Vikoflex 7170, (a coupling agent comprising epoxidized soybean oil sold by Viking Chemical Co.) was charged

to the reactor. After completion of the coupling reaction, the reaction was terminated by adding CO₂ and 0.2 phm water. The block copolymers were stabilized by adding 0.25 phm Irganox 1076 and 1.0 phm tris(nonyl-phenyl) phosphite to the reaction mixture.

The block copolymers and blends exhibited melt flows in the range of from 5 g/10 min. to 15 g/10 min. measured according to ASTM D-1238, condition G. The block copolymers and blends exhibited an Izod impact strength greater than 0.3 ft #/in. measured according to ASTM D-256. Blueness, tristimulus value "b", a measure of blue and yellow tint, was measured with a Hunter Lab Color Difference Meter 25 DM using three injection molded (350° F./30 tons/2 minutes) resin disks of 0.15 inch thickness and 2.5 inch diameter. Measurements were against a black background. A positive number represents yellow and a negative number represents blue.

Terms used in Table 27 are defined as follows:

S is styrene monomer in phm

i is n-butyllithium initiator in phm

B is 1,3-butadiene in phm

CA is epoxidized soybean oil coupling agent in phm

T is tetrahydrofuran in phm

Blend is 60 weight percent block copolymer (75S/25B) and 40 weight percent polystyrene

TABLE 27

Run	Blueness
<u>Block Copolymer containing 88 weight % S</u>	
101 0.04T, 40S, 0.03i, 0.02i, 20S, 5B/5S, 0.10i, 16S, 7B/7S, 0.41CA	-1.7
<u>Block Copolymer containing 85 weight % S</u>	
102 0.04T, 40S, 0.03i, 0.03i, 20S, 0.10i, 10S, 15S, 15B, 0.43CA	-1.8
103 0.04T, 40S, 0.03i, 0.03i, 20S, 0.10i, 10S, 15B/15S, 0.43CA	-2.4
104 0.3T, 40S, 0.03i, 0.02i, 20S, 0.04i, 10S, 15B/15S, 0.43CA	-4.3
<u>Block Copolymer containing 70 weight % S</u>	
105 0.04T, 37S, i, i, 19S, 9B, i, 14S, 21B, 0.41CA	-13.3
<u>Blend containing 85 weight % S</u>	
106 Block Copolymer/Polystyrene Blend	-11.7
107 Block Copolymer/Polystyrene Blend	-10.5
108 Block Copolymer/Polystyrene Blend	-15.6

The results in Table 27 indicate lower blueness values for inventive polymers in Runs 101-104. compared to

similar block copolymers containing 70 weight % styrene or block copolymer/polystyrene blends containing 85 weight % styrene. The odor of styrene monomer was observed in the copolymer/polystyrene blends, Runs 106-108. The odor was not observed in Runs 101-105.

Example XII

Conjugated diene/monovinylarene Block Copolymers 1 and 2 were prepared by sequential solution polymerizations employing three initiator charges, three styrene charges, and at least one butadiene charge, where at least two styrene charges precede the butadiene charge. The temperature peaked at about 110° C. after each monomer charge and polymerization was allowed to continue to substantial completion. Following completion of the sequential polymerizations, Vikoflex 7170, (a coupling agent comprising epoxidized soybean oil solid by Viking Chemical Co.) was charged to the reactor. The sequence of addition and relative amount of each charge is outlined below. S is styrene, B is butadiene, i is n-butyllithium initiator, and CA is coupling agent.

Block Copolymer 2 and Polystyrene 555, available from Novacor Plastics Division, were blended to form Polymer Blend 3.

1. Block Copolymer containing 85 weight % S 40S, i, i, 15S, 5B/5S, i, 10S, 10B/15S, CA
2. Block Copolymer containing 75 weight % S 40S, i, i, 20S, 7.5B, i, 15S, 17.5B, CA
3. Polymer Blend Containing 85 weight % S in the final Blend 60 weight % Block Copolymer 2 40 weight % Polystyrene

Block Copolymer 1 and Polymer Blend 3, each containing 85 weight % styrene in the final composition, were tested for free styrene monomer and other residual organic compounds using gas chromatography. The results are tabulated in the table below. In Table 28, ppm is parts per million.

TABLE 28

	Block Copolymer 1	Polymer Blend 3
Toluene	1 ppm	2 ppm
Vinylcyclohexene	3 ppm	1 ppm
Ethylbenzene	0 ppm	1 ppm
Isopropylbenzene	0 ppm	1 ppm
n-Propylbenzene	0 ppm	0 ppm
Styrene Monomer	0 ppm	128 ppm

The data in Table 28, clearly indicate no free styrene monomer detected in Block Copolymer 1 containing 85 % styrene compared to 128 ppm free styrene monomer in Polymer Blend 3 also containing 85 % styrene. The results are consistent with the observations noted in Example XI.

While the polymers and methods of this invention have been described in detail for the purpose of illustration, the inventive polymers and methods are not to be construed as limited thereby. This patent is intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed is:

1. A method for preparing a block copolymer comprising:

sequentially contacting under polymerization conditions at least one monovinylarene monomer, an organomonoalkali metal initiator, at least one conjugated diene monomer; and

thereafter coupling with a polyfunctional coupling agent to form said block copolymer;

wherein said initiator is provided in at least three initiator charges;

wherein said at least one monovinylarene monomer contains from 8 to 18 carbon atoms and is provided in at least three monovinylarene monomer charges; wherein said at least one conjugated diene monomer contains from 4 to 12 carbon atoms and is provided in at least one conjugated diene monomer charge; wherein at least three monovinylarene monomer charges precede the first charge containing said at least one conjugated diene monomer.

2. A method as recited in claim 1 having a charge sequence as follows;

- (a) initiator and monovinylarene monomer,
- (b) initiator and monovinylarene monomer,
- (c) initiator and monovinylarene monomer,
- (d) conjugated diene monomer, and
- (e) coupling agent.

3. A method as recited in claim 1 having a charge sequence as follows;

- (a) initiator and monovinylarene monomer,
- (b) initiator and monovinylarene monomer,
- (c) initiator and monovinylarene monomer,
- (d) conjugated diene monomer/monovinylarene monomer mixture, and
- (e) coupling agent.

4. A method as recited in claim 1 having a charge sequence as follows:

- (a) initiator and monovinylarene monomer,
- (b) initiator and monovinylarene monomer,
- (c) initiator and monovinylarene monomer,
- (d) conjugated diene monomer/monovinylarene monomer mixture,
- (e) conjugated diene monomer/monovinylarene monomer mixture, and
- (f) coupling agent.

5. A method according to claim 1 wherein at least four monovinylarene monomer charges precede the first charge containing conjugated diene monomer.

6. A method as recited in claim 5 having a charge sequence as follows;

- (a) initiator and monovinylarene monomer,
- (b) initiator and monovinylarene monomer,
- (c) initiator and monovinylarene monomer,
- (d) monovinylarene monomer,
- (e) conjugated diene monomer, and
- (f) coupling agent.

7. A method according to claim 1 wherein said monomers are added in an amount in the range of about 55 to about 95 weight percent monovinylarene monomer and about 5 to about 45 weight percent conjugated diene monomer.

8. A method according to claim 7 wherein said monomers are added in an amount in the range of about 60 to about 95 weight percent monovinylarene monomer and about 5 to about 40 weight percent conjugated diene monomer.

9. A method according to claim 8 wherein said monomers are added in an amount in the range of about 80 to about 95 weight percent monovinylarene monomer and about 5 to about 20 weight percent conjugated diene monomer.

10. A process according to claim 1 wherein the first monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 30 weight percent to about 50 weight per-

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cent based on the total weight of the final block copolymer.

11. A process according to claim 1 wherein the second monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 15 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

12. A process according to claim 1 wherein the third monovinylarene monomer charge contains monovinylarene monomer in the range of from about 5 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

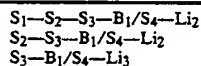
13. A process according to claim 5 wherein the third and fourth monovinylarene monomer charges each contain monovinylarene monomer in the range of from about 5 weight percent to about 20 weight percent based on the total weight of the final block copolymer.

14. A method according to claim 1 wherein each said monovinylarene monomer contains 8 to 12 carbon atoms and each said conjugated diene contains 4 to 6 carbon atoms.

15. A method according to claim 1 wherein said conjugated diene monomer is 1,3-butadiene and said monovinylarene monomer is styrene.

16. A monovinylarene/conjugated diene block copolymer comprising;

about 55 to about 95 weight percent polymerized monovinylarene based on the total weight of said copolymer and about 5 to about 45 weight percent polymerized conjugated diene based on the total weight of said copolymer;
said copolymer having polymer chains which result from coupling block copolymer chains



wherein

S=monovinylarene block
B=conjugated diene block

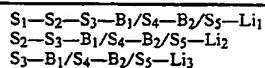
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B/S=tapered block of conjugated diene and monovinylarene

Li=living polymer site or coupling site.

17. A monovinylarene/conjugated diene block copolymer comprising;

about 55 to about 95 weight percent polymerized monovinylarene based on the total weight of said copolymer and about 5 to about 45 weight percent polymerized conjugated diene based on the total weight of said copolymer;
said copolymer having polymer chains which result from coupling block copolymer chains



wherein

S=monovinylarene block

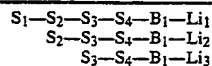
B=conjugated diene block

B/S=tapered block of conjugated diene and monovinylarene

Li=living polymer site or coupling site.

18. A monovinylarene/conjugated diene block copolymer comprising;

about 55 to about 95 weight percent polymerized monovinylarene based on the total weight of said copolymer and about 5 to about 45 weight percent polymerized conjugated diene based on the total weight of said copolymer;
said copolymer having polymer chains which result from coupling block copolymer chains



wherein

S=monovinylarene block

B=conjugated diene block

Li=living polymer site or coupling site.

* * * * *



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United States Patent [19]
Moczygemba et al.

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[45] **Date of Patent:** **Jan. 6, 1998**

[54] **BLOCK COPOLYMERS OF
MONOVINYLARENES AND CONJUGATED
DIENES AND PREPARATION THEREOF**

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[60] Continuation of Ser. No. 424,020, Apr. 18, 1995, abandoned, which is a division of Ser. No. 308,240, Sep. 19, 1994, Pat. No. 5,436,298, which is a continuation-in-part of Ser. No. 130,039, Sep. 30, 1993, abandoned.

[51] **Int. Cl.⁶** C08F 297/04; C08L 53/02

[52] **U.S. Cl.** 525/314; 525/89; 525/250;
525/271

[58] **Field of Search** 525/314, 89, 250,
525/271

[56] **References Cited**

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[57] **ABSTRACT**

A method for preparing resinous polymodal monovinylarene-conjugated diene block copolymers and polymers produced thereby are provided. The method comprises sequentially contacting under polymerization conditions:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a sequence of at least two charges selected from the group consisting of (i) initiator and a monovinylarene monomer, (ii) a mixture of monovinylarene monomer and conjugated diene monomer, (iii) a conjugated diene monomer, (iv) a monovinylarene monomer;

- (d) a coupling agent;
wherein the sequence of at least two charges in step (c) can be made in any order. In a preferred embodiment, at least three Initiator charges are provided. In another preferred embodiment, at least three monovinylarene charges precede the first charge containing conjugated diene. In another preferred embodiment, at least four monovinylarene charges precede the first charge containing conjugated diene.

18 Claims, No Drawings

BLOCK COPOLYMERS OF MONOVINYLARENES AND CONJUGATED DIENES AND PREPARATION THEREOF

This application is a continuation of application Ser. No. 08/424,020, filed Apr. 18, 1995, now abandoned, which is a division of application Ser. No. 08/308,240, filed Sep. 19, 1994, now U.S. Pat. No. 5,436,298, which is a continuation-in-part of application Ser. No. 08/130,039, filed Sep. 30, 1993, now abandoned.

FIELD OF THE INVENTION

This invention relates to block copolymers of monovinylarenes and conjugated dienes and methods of preparation of these block copolymers.

BACKGROUND OF THE INVENTION

There has developed in the polymer field, and especially in the packaging and related industries, a need for thermoplastic polymers that can be formed into odorless, colorless, transparent articles having good impact strength and ductility. There are needs for polymers which are useful as single components as well as for use in blends with other commonly used polymers to make articles with improved properties. The polymers satisfying these needs should be suitable for use with conventional extrusion, injection and blow molding equipment and also suitable for use in other methods of forming plastics into containers, tubes, films, fibers, and the like.

Much effort has been directed to the preparation of substantially transparent block copolymer resins with a variety of block structures produced by a variety of monomer addition sequences and a variety of coupling agents. Desirable properties and an economic advantage can be obtained by blending many monovinylarene-conjugated diene copolymers with polystyrene polymers. However, because blends of monovinylarene-conjugated diene copolymers with polystyrene polymers often contain unreacted styrene monomer, there is a need for high styrene content thermoplastic polymers which do not have undesirable unreacted styrene monomer while maintaining a good balance of physical and mechanical properties.

Odor caused by presence of unreacted styrene monomer in articles formed from various copolymers and blends of copolymers with polystyrene is a long-standing problem in applications where odorless, colorless materials which also have good impact strength and ductility are desirable. Specific examples include materials for water and food containers.

SUMMARY OF THE INVENTION

It is an object of this invention to provide novel resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes from which can be made transparent articles with an advantageous balance of properties including acceptable impact strength and ductility.

It is another object of this invention to provide novel resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes suitable for use as a replacement for blends of monovinylarene-conjugated diene copolymers with polymers of styrene. Further, it is an object to provide high styrene content resinous block copolymers of monovinylarene hydrocarbons and conjugated dienes which can be used for applications requiring absence of unreacted styrene monomer and from which can be made articles having good

impact strength and/or ductility and a good balance of other physical properties.

A further object of this invention is to provide novel processes for making resinous block monovinylarene-conjugated diene copolymers, including copolymers suitable for use in the place of polymer blends.

We have discovered a method of preparing a block copolymer comprising sequentially contacting under polymerization conditions:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a sequence of at least two charges selected from the group consisting of
 - (i) initiator and a monovinylarene monomer;
 - (ii) a mixture of monovinylarene monomer and conjugated diene monomer;
 - (iii) a conjugated diene monomer; and
 - (iv) a monovinylarene monomer;
- (d) a coupling agent;

wherein said sequence of at least two charges in step (c) can be made in any order. In a preferred embodiment, at least three initiator charges are provided. In another preferred embodiment, at least three monovinylarene charges precede the first charge containing conjugated diene. In still another preferred embodiment, at least four monovinylarene charges precede the first charge containing conjugated diene.

The polymers of this invention are transparent, colorless resins from which can be made articles with a good balance of properties such as impact strength and/or ductility. Invention polymers with high styrene content can be used as replacements for blends of other monovinylarene-conjugated diene copolymers with polystyrene and have the advantage of having minimal amounts of unreacted styrene monomer.

DETAILED DESCRIPTION OF THE INVENTION

This is a continuation-in-part of application Ser. No. 08/130,039 filed Sep. 30, 1993 the disclosure of which is herein incorporated by reference.

We have discovered novel monovinylarene-conjugated diene block copolymers which can be used neat as a substitute for blends of other monovinylarene-conjugated diene copolymers with polystyrene to produce resins which can be formed into high styrene content articles with low unreacted styrene monomer content and advantageous impact properties and/or ductility.

The polymers of this invention are characterized as resinous non-rubbery block copolymers of at least one conjugated diene with at least one monovinylarene and are prepared so that, when the choice of coupling agent permits at least a portion of the final product is of a branched, coupled character.

The polymers prepared according to this invention contain from about 55 to about 95, preferably from about 60 to about 95, more preferably from about 65 to about 95, weight percent copolymerized monovinylarene monomer based on the weight of total monomers employed.

Correspondingly, the inventive copolymers contain from about 45 to about 5, preferably from about 40 to about 5, and more preferably from about 35 to about 5 weight percent copolymerized conjugated diene monomer based on the total weight of monomers in the copolymer.

Presently preferred when the invention copolymers are used as replacements for blends of other monovinylarene-

conjugated diene copolymers with polystyrene, the polymers of this invention contain from about 80 to about 95, more preferably from 80 to 90 weight percent copolymerized monovinylarene monomer based on the weight of total monomers employed. Correspondingly, the inventive copolymers contain from about 20 to about 5, more preferably from about 20 to about 10 weight percent copolymerized conjugated diene monomer based on the total weight of monomers in the copolymer.

Generally, the first monovinylarene monomer charge contains monovinylarene monomer in the amount in the range of from about 30 weight percent to about 50 weight percent based on the total weight of the final block copolymer.

Generally, the second monovinylarene monomer charge contains monovinylarene monomer in the amount in the range of from about 15 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

When employed, the third monovinylarene monomer charge typically contains monovinylarene monomer in the amount in the range of from about 5 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

Under certain circumstances, it is desirable to provide a fourth monovinylarene monomer charge. If a fourth monovinylarene monomer charge is employed, the third and fourth monovinylarene monomer charges each contain monovinylarene monomer in the range of from about 5 weight percent to about 20 weight percent based on the total weight of the final block copolymer.

More particularly, with reference to the Summary of the Invention, the following embodiments are provided comprising or consisting essentially of the following sequences. In one embodiment the sequence of charges is (c) is (i), (ii). In a second embodiment, the sequence of charges in (c) is (ii), (iv). In a third embodiment, the sequence of charges in (c) is (i), (iv), (iii). In a fourth embodiment, the sequence of charges in (c) is (i), (ii), (ii). In a fifth embodiment the sequence of charges in (c) is (ii), (i), (ii). In a sixth embodiment the sequence of charges in (c) is (i), (iii).
Components

The process of this invention can be carried out using as an initiator any of the organomonoalkali metal compounds of the formula RM wherein R is an alkyl, cycloalkyl or arylcarbanion containing 4 to 8 carbon atoms and M is an alkyl metal cation. Mixtures of organoalkali metal compounds can be used. The presently preferred initiators are alkylmonolithium compounds, especially n-butyllithium or sec-butyllithium.

The conjugated diene monomers which can be used contain 4 to 6 carbon atoms and include 1,3-butadiene, 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene and mixtures thereof. Each of the charges containing conjugated diene in the same sequence of charges may be the same, but is not necessarily the same, conjugated diene monomer or mixture of conjugated dienes monomers. The presently preferred conjugated diene monomer is 1,3-butadiene.

The monovinylarene monomers which can be used contain 8 to 12 carbon atoms and include styrene, alpha-methylstyrene, 4-methylstyrene, 3-methylstyrene, 2-methylstyrene, 4-ethylstyrene, 3-ethylstyrene, 2-ethylstyrene, 4-tert-butylstyrene, 2,4-dimethylstyrene and condensed aromatics such as vinyl naphthalene and mixtures thereof. Each of the charges containing monovinylarene monomer in the same sequence of charges may be the same,

but is not necessarily the same, monovinylarene monomer or mixture of monovinylarene monomers. The presently preferred monovinylarene monomer is styrene.

Examples of polar compounds which can be advantageously employed as randomizers and promoters are ethers, thioethers (sulfides) and tertiary amines. It is usually preferred to use ethers and sulfides in which the radicals attached to the oxygen or sulfur atoms are hydrocarbon radicals. It is to be understood also that mixtures of polar compounds can be employed in the practice of the present invention. Presently preferred are either tetrahydrofuran or diethyl ether.

Among the suitable coupling agents are the di- or multivinylarene compounds, di- or multiepoxides, di- or multisocyanates, di- or multiimines, di- or multialdehydes, di- or multiketones, alkoxytin compounds, di- or multihalides, particularly silicon halides and halosilanes, mono-, di-, or multianhydrides, mono-, di-, or multiesters, preferably the esters of monoalcohols with polycarboxylic acids, diesters which are esters of monohydric alcohols with dicarboxylic acids, lactones, monobasic acids with polyalcohols such as glycerol, and the like, including compounds containing two or more of these groups and mixtures of two or more compounds.

Useful multifunctional coupling agents include epoxidized vegetable oils such as epoxidized soybean oil, epoxidized linseed oil and the like or mixtures thereof.

The presently preferred coupling agent is epoxidized vegetable oil. Presently preferred is epoxidized soybean oil.
Process

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a first embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a second embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and a subsequent addition of a second charge of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, which is in turn followed by a charge of monovinylarene monomer, and a subsequent coupling step. Sheet made from such copolymer has a glossy hard surface and has excellent impact resistance.

The unique polymodal block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a third embodiment of this invention are produced by the unique sequence of three sequential charges of monovinylarene monomer and initiator, a subsequent addition of a charge of monovinylarene monomer, followed by a separate charge of a conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a fourth embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by two separate sequential charges of a mixture of monovinylarene monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a fifth embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of a sequential charge of initiator and monovinylarene monomer, followed by a separate charge of a mixture of monovinylarene monomer and conjugated diene, followed by a sequential charge of initiator and monovinylarene monomer, followed by a charge of a mixture of monovinyl monomer and conjugated diene, and a subsequent coupling step.

The unique polymodal tapered block character of the polymer and good impact strength and/or ductility of articles made from the polymer of a sixth embodiment of this invention are produced by the unique sequence of an initial charge of monovinylarene monomer and initiator and subsequent addition of two separate sequential charges of initiator and monovinylarene monomer, followed by a separate charge of conjugated diene, and a subsequent coupling step.

In each of the embodiments of this invention the first initiator charge produces active living monovinylarene component polymer blocks with alkali metal atoms (from the initiator) on at least one end to form active reaction sites. The other ends of each of these polymeric chains will be end-capped with the "organo" portion of the organomonoalkali metal compound used as the initiator, i.e., the R portion of the RM compound. Each subsequent monomer charge adds monomer to the living polymer chain at the alkali metal reaction site. At each stage of charging, polymerization is usually allowed to continue until essentially no free monomer is present.

With each subsequent charge which includes initiator a new polymer-alkali metal species will be produced, and each subsequent monomer charge has an opportunity for polymerization of part of the charge with each of the existing polymer-alkali metal species. After virtually complete polymerization of the final monomer charge, the active living linear block copolymers are charged with a difunctional or polyfunctional coupling agent to allow coupling of each of the living species with each of the other living species or with others of the same living species to form the desired polymodal block copolymers. If the coupling agent is not 100 percent efficient and/or if less or more than a stoichiometric amount of coupling agent is used, there can be some uncoupled terminated polymer chains of each of the species in the final reaction mixture.

Use of difunctional coupling agents will produce predominantly linear polymer chains. Depending upon amount and functionality, various degrees and kinds of branching may be accomplished with polyfunctional coupling agents.

The charging sequences of the various embodiments of this invention and the resulting polymers at each stage are exemplified using a selected monovinylarene monomer, conjugated diene and polyfunctional coupling agent in the following Tables 1-4. The "Organo" end caps are disregarded in designation of the terminal blocks because the end caps are so small in relation to the polymer chains that they do not contribute to the properties of the resulting polymodal polymers.

TABLE 1

Invention Charging Sequence (First Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ -Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ -S ₂ -Li ₁ S ₂ -Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ -S ₂ -S ₃ -Li ₁ S ₂ -S ₃ -Li ₂ S ₃ -Li ₃
(d)	butadiene ₁ and styrene ₄	S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -Li ₁ S ₂ -S ₃ -B ₁ /S ₄ -Li ₂ S ₃ -B ₁ /S ₄ -Li ₃
(e)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where S = styrene

B = butadiene

B/S = tapered block monovinylarene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.
subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 2

Invention Charging Sequence (Second Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ -Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ -S ₂ -Li ₁ S ₂ -Li ₂
(c)	butadiene ₁ and styrene ₃	S ₁ -S ₂ -B ₁ /S ₃ -Li ₁ S ₂ -B ₁ /S ₃ -Li ₂
(d)	styrene ₄	S ₁ -S ₂ -B ₁ /S ₃ -S ₄ -Li ₁ S ₂ -B ₁ /S ₃ -S ₄ -Li ₂
(e)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where S = styrene

B = butadiene

B/S = tapered block monovinylarene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.
subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 3

Invention Charging Sequence (Third Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ -Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ -S ₂ -Li ₁ S ₂ -Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ -S ₂ -S ₃ -Li ₁ S ₂ -S ₃ -Li ₂ S ₃ -Li ₃
(d)	styrene ₄	S ₁ -S ₂ -S ₃ -S ₄ -Li ₁ S ₂ -S ₃ -S ₄ -Li ₂ S ₃ -S ₄ -Li ₃

TABLE 3-continued

Invention Charging Sequence (Third Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(e)	butadiene ₁	S ₁ -S ₂ -S ₃ -S ₄ -B ₁ -Li ₁ S ₂ -S ₃ -S ₄ -B ₁ -Li ₂ S ₃ -S ₄ -B ₁ -Li ₃
(f)	coupling agent	polymodal block copolymers with styrene terminal blocks

where S = styrene

B = butadiene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.
subscripts = designation of the numerical order in which that particular component was charged or formed.

TABLE 4

Invention Charging Sequence (Fourth Embodiment)		
Charge	Contents of Charge	Resulting Polymer Chains
(a)	randomizer, initiator ₁ and styrene ₁	S ₁ -Li ₁
(b)	initiator ₂ and styrene ₂	S ₁ -S ₂ -Li ₁ S ₂ -Li ₂
(c)	initiator ₃ and styrene ₃	S ₁ -S ₂ -S ₃ -Li ₁ S ₂ -S ₃ -Li ₂ S ₃ -Li ₃
(d)	butadiene ₁ and styrene ₄	S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -Li ₁ S ₂ -S ₃ -B ₁ /S ₄ -Li ₂ S ₃ -B ₁ /S ₄ -Li ₃
(e)	butadiene ₂ and styrene ₅	S ₁ -S ₂ -S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₁ S ₂ -S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₂ S ₃ -B ₁ /S ₄ -B ₂ /S ₅ -Li ₃
(f)	coupling agent	polymodal tapered block copolymers with styrene terminal blocks

where S = styrene

B = butadiene

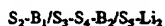
B/S = tapered block monovinylarene

Li = residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.
subscripts = designation of the numerical order in which that particular component was charged or formed.

Fifth Embodiment Sequence;

- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,
- conjugated diene monomer/monovinylarene monomer mixture,
- initiator and monovinylarene monomer.
- conjugated diene monomer/monovinylarene monomer mixture, and
- coupling agent.

Resulting Polymer Chains



where

S=styrene

B=butadiene

B/S=tapered block

Li=residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts=designation of the numerical order in which that particular component was charged or formed.

Sixth Embodiment Sequence;

- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,
- initiator and monovinylarene monomer,
- conjugated diene monomer, and
- coupling agent.

Resulting Polymer Chains



where

S=styrene

B=butadiene

Li=residue from a monoalkali metal initiator remaining on the end of the polymerization chain or reaction site prior to termination or coupling.

subscripts=designation of the numerical order in which that particular component was charged or formed.

In each of the embodiments the randomizer is usually added with the hydrocarbon diluent initially charged to the reactor. Each of the charges which has two monomers may be either a mixture of the two monomers or simultaneous charging of two separate monomers.

As can be seen from the intermediate products listed in the charging sequence tables above, in each of the embodiments of the invention there are at least two distinct species of polymer chains before coupling. The first and third through sixth embodiments have at least three distinct species of polymer chains before coupling. Thus, polymodal block copolymers comprising various proportions of relatively high, intermediate and low molecular weight species can be produced.

Tapered blocks in each of the growing polymer chains of embodiments having tapered blocks are produced by simultaneously charging with at least two monomers as shown in the preceding tables of the inventive charging sequences. The randomizer regulates tapering or random polymerization of the monovinylarene monomer and the conjugated diene in a mixed monomer charge. Choice of randomizer can be used to manipulate the degree and direction of taper in blocks resulting from charges of mixtures of monomers. The taper can be either a graduation from conjugated diene rich chain to monovinylarene rich chain or a graduation from a monovinylarene rich chain to conjugated diene rich chain according to preference of the initiator-randomizer complex for one type of monomer over the other.

The weight ratio of monovinylarene monomer to conjugated diene monomer in each of the tapered blocks is from about 1:0.63 to about 1:2, preferably from about 1:0.67 to about 1:1.8, and more preferably from about 1:0.8 to about 1:1.5. In the fourth embodiment, the weight ratios of monovinylarene monomer to conjugated diene monomer in each of the tapered blocks in the same polymer chain do not have to be the same.

The polymerization process is carried out in a hydrocarbon diluent at any suitable temperature in a range of about

-10° to about 150° C., preferably in the range of about 0° to about 110° C., at pressures sufficient to maintain the reaction mixture substantially in the liquid phase. Charges of monomer and initiator are made in the presence of an amount of diluent or solvent sufficient to prevent excessive heat of reaction. Temperatures and pressures will peak during polymerization of each monomer charge and then decrease when essentially no free monomer is left to react. Appropriate hydrocarbon diluents include linear and cycloparaffins such as butane, pentane, hexane, octane, cyclohexane, cyclopentane and mixtures thereof. Presently preferred is cyclohexane. Generally the choice of hydrocarbon or hydrocarbon mixture and the temperature is such that the resulting polymer is in solution.

Small amounts of polar compounds are used to improve the effectiveness of alkylmonoalkali metal initiators such as n-butyllithium; dissociation of the alkylmonoalkali metal initiators affects the rate of initiation and polymerization. The polar compounds also effect partial randomization of the vinylarene/conjugated diene so as to increase the random portion of the tapered block. The polar compounds are generally used in admixture with the hydrocarbon diluent.

The amounts of polar compounds used as randomizers and promoters of effectiveness of initiators in this invention will vary according to the reactivity and effectiveness of the particular randomizer used. The amounts of polar compounds used as randomizers will also vary according to the desired molecular structure of the portions of tapered blocks which result from conjugated diene addition. For example, when using tetrahydrofuran, and polymers with higher vinyl character resulting from 1.2 addition in excess of 1.4 addition are desired, larger amounts of tetrahydrofuran are used. However, use of too much randomizer can result in excessive polymer-lithium termination during polymerization and/or poor stability of the polymer and/or undesired side reactions, depending upon choice of randomizer. Use of too little randomizer would result in inefficient initiator use, compositional variations and broader molecular weight distribution.

The initial monovinylarene charge is made with the randomizer present for the additional effect of causing the monovinylarene component resulting from each initiator charge to be of relatively narrow molecular weight distribution. In each of the embodiments of this invention, by varying the amounts of initiator in each of the charges having initiator, the differences in molecular weights of the monovinylarene components resulting from each of these charges can be increased.

In each of the embodiments of the invention, amounts of initiator employed are those which will produce resins with desirable melt flow which can be used to make articles with a good balance of properties including minimal blueness, and good impact strength and/or ductility. Presently preferred when making invention polymers to be used as replacements for blends of other block copolymers with polystyrene are amounts of initiator in each of the initiator charges sufficient to obtain a block copolymer having a melt flow in the range from about 2 to about 50 g/10 minutes, more preferably from about 4 to about 30 g/10 minutes, and most preferably from about 7 to about 20 g/10 minutes, as determined by ASTM D1238-73, condition 200° C./5.0 kg. The amounts of initiator contemplated as useful in each of the charges having initiator are shown in Tables 5 through 8.

Use of too small an amount of initiator would result in high molecular weight polymers. Conversely, use of too large an amount of initiator would result in polymers having short chain polymeric species and low molecular weight.

Varying the weight ratios of amounts of each of the initiator charges made in each polymerization will result in variations of the proportionate amounts of species present in the copolymer. Other factors affecting the proportionate amounts of species present in the copolymer include presence of impurities and/or scavengers in the reactor, effectiveness of the polar randomizer as a promoter and choice of coupling agent(s).

In any of the embodiments of this invention it is feasible to stretch out over an interval of time the addition of one or more of the increments of initiator, thus spreading (increasing) further the polymodality of the resulting product upon coupling.

The polymerization is carried out in a substantial absence of oxygen and water, preferably under an inert gas atmosphere. Prior to the coupling step, the reaction mass contains a very high percentage of molecules (polymer chains) in which an alkali metal cation is positioned at one end of each polymer chain. Impurities in the feed such as water or alcohol reduce the amounts of monoalkali metal polymer in the reaction mass.

After essentially complete polymerization of the final charge added to the polymer, one or more suitable difunctional or polyfunctional coupling agents is added. As used here, the term "coupling" means the bringing together and joining, by means of one or more central coupling atoms or coupling moieties, two or more of the living monoalkali metal-terminated polymer chains.

Any effective amount of the coupling agent can be employed. While the amount is not believed to be particularly critical, a stoichiometric amount relative to the active polymer-alkali metal tends to promote maximum coupling as a generality. Presently preferred is an amount of coupling agent slightly greater than stoichiometric relative to the active polymer-alkali metal. However, less than stoichiometric amounts can be used for higher degrees of coupling where desired for particular products of broadened molecular weight distribution.

Typically, in each of the embodiments of this invention, the total amount of coupling agent is in the range of about 0.005 to 10 phm (parts per 100 parts of total monomers employed in the polymerization). Preferred when most combinations of monomers and coupling agents are used to practice this invention is about 0.2 to about 0.6 phm of coupling agent, depending on amounts of initiator used. Presently most preferred is about 0.3 to about 0.5 phm, depending upon amounts of initiator used. Use of an insufficient amount of coupling agent will result in less complete coupling of the living polymer chains or, depending upon choice of coupling agent, more branching; use of an excessive amount of coupling agent will also result in more uncoupled chains.

At the conclusion of the coupling process, the coupled polymer may still contain bound polymeric alkali metal alkoxides depending on the type of coupling agent employed. The system is treated with an active compound such as water, alcohol, phenols, carbon dioxide or linear saturated aliphatic mono- and dicarboxylic acids to remove any remaining alkali metal from the copolymer chain.

Stabilization agents can be added to provide oxidative stability for the polymer during processing and handling and subsequent long term use by the customer. Commonly used stabilization processes can use a combination of compounds which include, but are not limited to, a hindered phenol and an organophosphite, particular examples of which are octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate and tris-nonylphenylphosphite.

After stabilization, the hydrocarbon diluent is then flashed from the polymer solution to increase the solids content. Flashing of the polymer cement may be followed by desolventizing extrusion with vacuum in commercial production or by other vacuuming processes to achieve consistent solvent content of less than 0.3 weight percent.

The resinous copolymeric products can be, and normally are, compounded with anti-oxidants, anti-blocking agents, release agents and other additives, as known in the compounding arts.

Typical charging sequences and useful ranges of amounts of the charges for each of the first four embodiments of this invention are given in Tables 5 through 8. The amounts of initiator and randomizer indicated in the Table for each charge are also appropriate for the fifth and sixth embodiments.

TABLE 5

Ranges of Amounts of Components in a Typical Invention Charging Sequence* (First Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(a)	randomizer ^c initiator and monovinylarene monomer	0.001-3.0 0.001-0.20	0.01-1.0 0.005-0.10	0.02-0.5 0.01-0.07
(b)	monovinylarene monomer initiator and monovinylarene monomer	32-48 12-28	35-45 15-25	38-42 18-22
(c)	monovinylarene monomer initiator and monovinylarene monomer	0.001-0.20	0.005-0.15	0.01-0.12
(d)	monovinylarene monomer and conjugated diene monomer	6-14 5-25	8-12 10-20	9-11 13-17
(e)	coupling agent	5-25	10-20	13-17
		0.15-0.35	0.18-0.32	0.20-0.30

*Monomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 6

Ranges of Amounts of Components in a Typical Invention Charging Sequence* (Second Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(a)	randomizer ^c initiator and monovinylarene monomer	0.001-3.0 0.001-0.20	0.01-1.0 0.005-0.10	0.02-0.5 0.01-0.07
(b)	monovinylarene monomer initiator and monovinylarene monomer	32-48 12-28	35-45 15-25	38-42 18-22
(c)	monovinylarene monomer initiator and monovinylarene monomer	0.001-0.20	0.005-0.15	0.01-0.12
		6-14	8-12	9-11

TABLE 6-continued

Ranges of Amounts of Components in a Typical Invention Charging Sequence* (Second Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(d)	monovinylarene monomer and coupling agent	6-14	8-12	9-11
(e)		0.15-0.35	0.18-0.32	0.20-0.30

*Monomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 7

Ranges of Amounts of Components in a Typical Invention Charging Sequence* (Third Embodiment)				
Step	Component	Broad Range ^c	Preferred Range ^c	More Preferred Range ^c
(a)	randomizer ^c initiator and monovinylarene monomer	0.001-3.0 0.001-0.20	0.01-1.0 0.005-0.10	0.02-0.5 0.01-0.07
(b)	monovinylarene monomer initiator and monovinylarene monomer	32-48 12-28	35-45 15-25	38-42 18-22
(c)	monovinylarene monomer initiator and monovinylarene monomer	0.001-0.20	0.005-0.15	0.01-0.12
(d)	monovinylarene monomer and conjugated diene monomer	6-14 5-25	8-12 10-20	9-11 13-17
(e)	coupling agent	5-25	10-20	13-17
		0.15-0.70	0.18-0.60	0.20-0.50

*Monomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

TABLE 8

Ranges of Amounts of Components in a Typical Invention Charging Sequence* (Fourth Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
(a)	randomizer ^c initiator and monovinylarene monomer	0.001-3.0 0.001-0.20	0.01-1.0 0.005-0.10	0.02-0.5 0.01-0.07
(b)	monovinylarene monomer initiator and monovinylarene monomer	32-48 12-28	35-45 15-25	38-42 18-22
(c)	monovinylarene monomer initiator and monovinylarene monomer	0.001-0.20	0.005-0.15	0.01-0.12
(d)	monovinylarene monomer and	10-25	12-20	14-18
		2-10	3-7	4-6

TABLE 8-continued

Ranges of Amounts of Components in a Typical Invention Charging Sequence ^a (Fourth Embodiment)				
Step	Component	Broad Range ^b	Preferred Range ^b	More Preferred Range ^b
	conjugated diene monomer	2-10	3-7	4-6
(e)	monovinylarene monomer and conjugated diene monomer	3-12	5-9	6-8
(f)	coupling agent	0.15-0.70	0.18-0.60	0.20-0.50

^aMonomers within each charge having more than one monomer can be added simultaneously or as a mixture, slowly or quickly. Randomizer in charge (a) may be already present in the diluent or added as a separate charge.

^bRanges of amounts are given in parts by weight per 100 parts by weight of total monomers (phm).

^cTo achieve high vinyl content, up to 3 phm randomizer may be used.

After coupling at least the coupled and uncoupled polymeric species shown in Tables 9 through 12 are present in the polymodal polymers of the first through fourth embodiments, respectively, of this invention.

TABLE 9

Polymeric Species Included in First Embodiment	
$S_1-S_2-S_3-B_1/S_4-x-S_4$	
$B_1-S_2-S_3-S_1$	
$S_2-S_3-B_1/S_4-x-S_4/B_1-S_2-S_2$	
$S_2-B_1/S_4-x-S_4/B_1-S_2$	
$S_1-S_2-S_3-B_1/S_4-x-S_4/B_1-S_2-S_2$	
$S_1-S_2-S_3-B_1/S_4-x-S_4/B_1-S_2$	
$S_2-S_3-B_1/S_4-x-S_4/B_1-S_2$	
$S_1-S_2-S_3-B_1/S_4$	
$S_2-S_3-B_1/S_4$	
S_2-B_1/S_4	

S = monovinylarene block

B = conjugated diene block

B/S = tapered block monovinylarene

x = coupling moiety or coupling site

subscripts = indications of the charges which were the source of the polymer blocks.

TABLE 10

Polymeric Species Included in Second Embodiment	
$S_1-S_2-B_1/S_3-S_4-x-S_4-S_2$	
$B_1-S_2-S_1$	
$S_1-S_2-B_1/S_3-S_4-x-S_4-S_2/B_1-S_2$	
$S_2-B_1/S_3-S_4-x-S_4-S_2/B_1-S_2$	
S_2-B_1/S_3-S_4	
$S_1-S_2-B_1/S_3-S_4$	

S = monovinylarene block

B = conjugated diene block

B/S = tapered block monovinylarene

x = coupling moiety or coupling site

subscripts = indications of the charges which were the source of the polymer blocks.

TABLE 11

Polymeric Species Included in Third Embodiment	
$S_1-S_2-S_3-S_4$	
$B_1-x-B_1-S_4-S_3-S_2-S_1$	
$S_2-S_3-S_4-B_1-x-B_1-S_4-S_3-S_2$	
$S_2-S_4-B_1-x-B_1-S_4-S_3$	

TABLE 11-continued

Polymeric Species Included in Third Embodiment	
5	$S_1-S_2-S_3-S_4-B_1-x-B_1-S_4-S_3-S_2$
	$S_1-S_2-S_3-S_4-B_1-x-B_1-S_4-S_3$
	$S_2-S_3-S_4-B_1-x-B_1-S_4-S_3$
	$S_1-S_2-S_3-S_4-B_1$
	$S_2-S_3-S_4-B_1$
	$S_3-S_4-B_1$

S = monovinylarene block

B = conjugated diene block

x = coupling moiety or coupling site

subscripts = indications of the charges which were the source of the polymer blocks.

TABLE 12

Polymeric Species Included in Fourth Embodiment	
20	$S_1-S_2-S_3$
	$B_1/S_4-B_2/S_2-x-S_2$
	$B_2-S_2/B_1-S_2-S_2-S_1$
	$S_2-S_3-B_1/S_4$
	$B_2/S_2-x-S_2/B_2-S_4/B_1-S_2-S_2$
	$S_2-B_1/S_4-B_2/S_2-x-S_2/B_2-S_4/B_1-S_2$
	$S_1-S_2-S_3$
25	$B_1/S_4-B_2/S_2-x-S_2/B_2-S_4/B_1-S_2-S_2$
	$S_1-S_2-S_3$
	$B_1/S_4-B_2/S_2-x-S_2/B_2-S_4/B_1-S_2$
	$S_2-S_3-B_1/S_4-B_2/S_2-x-S_2$
	B_2-S_2/B_1-S_2
	$S_1-S_2-S_3-B_1/S_4-B_2/S_2$
	$S_2-S_3-B_1/S_4-B_2/S_2$
	$S_2-B_1/S_4-B_2/S_2$

S = monovinylarene block

B = conjugated diene block

B/S = tapered block monovinylarene

x = coupling moiety or coupling site

subscripts = indications of the charges which were the source of the polymer blocks.

In each of the embodiments, depending upon choice and amount of coupling agent or agents and whether coupling agents are charged as a mixture or incrementally, there can be present other polymeric species with varying degrees of branching.

Blends

The resinous polymodal copolymer products of this invention can be blended with other polymers such as polystyrene, acrylonitrile-butadiene-styrene copolymers (ABS), styrene-acrylonitrile copolymers (SAN), and other styrene copolymers. When less transparency is desired or transparency is not necessary, the invention copolymers can be blended with high impact polystyrene (HIPS) or polyolefins and/or olefin copolymers.

The compositions of this invention or blends thereof can be extruded, thermoformed, injection molded, blow molded, or made into films or sheets. The compositions of this invention can be used as high styrene content copolymer substitutes for blends of polystyrene with other monovinylarene-conjugated diene block copolymers in making articles with essentially no styrene monomer content. Non-inventive blends typically have 100-300 ppm residual styrene. Articles made from the compositions of this invention are transparent with low blueness, have good impact strength and have other physical properties within acceptable ranges for such applications as drinking cups, lids, bottles, other food containers, medical drainage units, shrink wrap and over-wrap.

Test Procedures

The blueness values (tristimulus value "b") were determined on a Model D 25 Hunter Lab Color Difference Heter

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using the Hunter Lab procedure. Blueness values are a measure of blue tint expressed as -b, where larger absolute numbers indicate more blueness. Generally, test specimens which exhibited -7.5 Hunter b blueness or less blueness were considered to have "low blueness". In each example, reported blueness (Hunter "b") values for injection molded test specimens are for the average of three readings on three stacked 0.050" by 2.5" diameter injection molded disks. Disks were injection molded at 350° F/30 tons/2 minutes. Measurements were made against a black background.

Impact characterization of the extruded sheets was done using an Elmendorf Tearing Tester (Thwing-Albert Instrument Co.) in a manner similar to Spencer Impact Testing defined by ASTM D 3420. However, since the 4" sheet width was not sufficient to fill the entire sample clamp, the values were considered to be only relative. A 3/8" diameter tip was used with a 3200 g weight in place. The orientation of the sheet was such that the sheet machine direction was parallel to the pendulum swing plane. The convex side of the sheet was up in all tests. Reported impact values are the average of five tests on the sheet and are considered unitless because of the relative nature of results of the test procedure used.

Other properties were tested using ASTM procedures as shown in Table 13.

TABLE 13

Test Procedures Used	
Property	ASTM Method
Flow rate, g/10 min	D 1238-88
Condition 200° C./5.0 kg	
Haze, %	D 1003-61 (1990)
Transmittance, %	D 1003-61 (1990)
Shore D hardness	D 2240-91
Tensile strength at yield and break, MPa	D 638-91 at 50 mm/min
Elongation at yield and break, %	Type I test specimens
Flexural modulus, MPa	D 638-91 at 50 mm/min
Flexural strength, MPa	D 790-86
Izod impact strength, notched, J/m	D 790-86
Vicat softening point, °C.	D 256-88
Total energy dart drop, J	D 1525-91
	D 4272-85

EXAMPLES

The following examples will describe in more detail the experimental process used and the polymodal block copolymers with vinylarene terminal blocks obtained as a result of invention processes. These examples should be taken as illustrative and not restrictive.

Styrene and butadiene were chosen as monomers to exemplify the invention, and randomizer, initiator, coupling agent and diluent appropriate for these monomers were used.

Example I

This example describes two invention polymerization runs (1, 2) which were made to exemplify the first embodiment of the invention. Polymerization was carried out in a stirred, 100-gallon carbon steel reactor with internal cooling coils. Sequential polymerizations were conducted under nitrogen employing essentially anhydrous reactants and conditions. Approximately 152 kg cyclohexane solvent (168.9 phm) were charged to the reactor. The tetrahydrofuran (THF) randomizer/promoter was in solution in the cyclo-

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hexane solvent initially charged to the reactor. The n-butyllithium initiator (from Lithium Corporation of America) was charged as a 2 weight percent solution in cyclohexane. The cyclohexane diluent containing the THF was preheated to about 40° C. before monomers were charged to the reactor. Monomers were styrene (from Sterling Chemical) and 1,3-butadiene (from Texas El Paso). Before charging, monomers were dried by passage over activated alumina (Kaiser A-201).

Reactants were charged to the reactor in the sequences and amounts indicated in Table 14. Lines were flushed with approximately 1.0 kg cyclohexane following each charge of monomer and with 0.5 Kg cyclohexane following each charge of initiator or additive. Polymerization was allowed to continue to completion after each monomer charge. Polymerization temperatures ranged from about 38° C. to about 110° C. and pressure ranged from about 2 psig to about 60 psig. Total monomer weight was about 90 kg.

After completion of the sequential polymerizations, Vikoflex® 7170, (a coupling agent comprising epoxidized soybean oil, available from Viking Chemical Company) was charged to the reactor. After completion of the coupling reaction, the reaction was terminated by adding 0.1 phm carbon dioxide and 0.2 phm water. The block copolymers were stabilized by adding a mixture containing 0.25 phm Irganox® 1076 (a hindered phenol commercially available from Ciba-Geigy) and 1.0 phm tris(nonylphenyl) phosphite (available as TNPP from GE Specialty Chemicals) to the reaction mixture. Each stabilizer was dissolved separately in cyclohexane and then the solutions were mixed together. Enough of the mixture was added to the reactor to provide 0.25 phm hindered phenol and 1 phm organic phosphite. In Runs 1 and 2 a microcrystalline wax (BE Square® 195) was also added as an antiblocking agent.

Substantially all of the remaining diluent was removed by passing the mixture through a Luwa Filmtruder at 155° C., with a residence time of approximately 2 minutes. The resulting polymer was stranded and pelletized in a devolatilizing extruder at about 155° C. with a residence time of approximately 3-4 minutes.

TABLE 14

Invention Runs - First Embodiment			
	Run 1	Run 2	
Step 1			
Cyclohexane, phm	168.9	168.9	
Tetrahydrofuran, phm	0.04	0.3	
n-Butyllithium initiator, phm	0.034	0.033	
Styrene, phm	40	40	
Cyclohexane, phm	1.7	1.7	
Peak Polymerization Temperature, °C.	91.6	94.6	
Peak Polymerization Pressure, psi	38.0	35.8	
Polymerization Time, min	4	3	
Step 2			
n-Butyllithium initiator, phm	0.030	0.022	
Styrene, phm	20	20	
Cyclohexane, phm	1.7	1.7	
Peak Polymerization Temperature, °C.	89.8	90.1	
Peak Polymerization Pressure, psi	36.4	37.0	
Polymerization Time, min	4	3	

TABLE 14-continued

Invention Runs - First Embodiment		
	Run 1	Run 2
<u>Step 3</u>		
n-Butyllithium, initiator, phm	0.040	0.040
Styrene, phm	10	10
Cyclohexane, phm	1.7	1.7
Peak Polymerization Temperature, °C.	83.8	84.6
Peak Polymerization Pressure, psi	36.8	37.5
Polymerization Time, min	3	2
<u>Step 4</u>		
Butadiene, phm	15	15
Styrene, phm	15	15
Cyclohexane, phm	2.2	2.2
Peak Polymerization Temperature, °C.	111.0	111.5
Peak Polymerization Pressure, psi	55.8	54.7
Polymerization Time, min	8	6
Polymer Analysis (prior to coupling) (GPC area composition)*		
Peak 1	139.3	151.0
Peak 2	58.9	72.6
Peak 3	37.0	44.6
<u>Step 5 (Coupling)</u>		
Vikoflex 7170, phm	0.27	0.25
Cyclohexane, phm	0.6	0.6
Temperature, °C.	99.3	98.4
Pressure, psi	50	50.5
<u>Step 6 (Terminating)</u>		
Water, phm	0.20	0.2
Carbon Dioxide, phm	0.17	0.17
<u>Step 7 (Stabilizing)</u>		
Stabilizer Mixture, phm	1.25	1.25
Antiblocking agent, phm	.18	.18
<u>Recovered Resin</u>		
Melt Flow, g/10 min	8.0	8.6

*Response of a dielectric detector in an Applied Automation process control GPC.

Injection molded test specimens of the block copolymers exhibited the properties shown in Table 15.

TABLE 15

Physical Properties of Injection Molded Articles (First Embodiment)		
Property	Invention Polymer 1	Invention Polymer 2
Melt flow, g/10 min	8.0	8.6
Haze, %	0.9	0.9
Hunter blueness, b	-2.42	-4.28
Shore D Hardness	77	75
Notched Izod impact, J/m	22.4	24.0
<u>Tensile strength</u>		
yield, MPa	44.7	42.3
break, MPa	28.0	28.6

TABLE 15-continued

Physical Properties of Injection Molded Articles (First Embodiment)		
Property	Invention Polymer 1	Invention Polymer 2
<u>Elongation</u>		
yield, %	5.42	5.09
break, %	89.8	68.3
Flexural modulus, MPa	1765	1724

Example II

This example describes four invention polymerization runs which were made to exemplify the second embodiment of the invention. Styrene (from Sterling Chemical) and 1,3-butadiene (from Texas El Paso) were dried by passage over activated alumina (Kaiser A-201), and then copolymerized and coupled in a 4-stage process using n-butyllithium initiator (from Lithium Corporation of America).

Polymerization runs were carried out under nitrogen in a stirred, jacketed, stainless steel 7.6-liter reactor employing essentially anhydrous reactants and conditions. The anhydrous mixtures were stirred continuously during the polymerization process. The cyclohexane diluent, which contained 0.04 phm tetrahydrofuran (THF) in each polymerization in this example, was preheated to about 50° C. before monomers were charged to the reactor. The n-butyllithium was charged as a 2 weight percent solution in cyclohexane. In the polymerization step in which both butadiene and styrene were charged, they were charged simultaneously as a mixture.

In the coupling step, the Vikoflex® 7170 coupling agent used was an epoxidized vegetable oil commercially available from Viking Chemical Company. In the terminating step, carbon dioxide from a pressurized container was admitted to provide about 0.4 phm carbon dioxide to the reactor. Water was also added in an amount slightly in stoichiometric excess of the initiator to separate the lithium residues from the polymer chains.

The antioxidant mixture added in the stabilizing step contained a hindered phenol [octadecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate, commercially available as Irganox® 1076 from Ciba-Geigy] and an organic phosphite (trisnonylphenyl phosphite, available as TNPP from GE Specialty Chemicals). Each stabilizer was dissolved separately in cyclohexane and mixed together. Enough of the mixture was added to the reactor to provide 0.25 phm hindered phenol and 1 phm organic phosphite. In all four runs, a microcrystalline wax (BE Square® 195) was also added as an antiblocking agent.

After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 3-20 phm cyclohexane solvent and cleared with a nitrogen purge.

Following the stabilization step, each copolymer solution was flashed at 178°-180° C. to remove a portion of the diluent. Substantially all of the remaining diluent was removed in a vacuum oven by drying at 90° C. for one hour. The resulting polymer was chopped in a granulator into crumb and then dried for an additional hour in a vacuum oven.

In each of the four runs (3, 4, 5 and 6), 1500 g total monomers (butadiene and styrene) were used. About 76 weight percent of the total amount of cyclohexane diluent

(3130 g) was charged initially. The remaining cyclohexane diluent was added during the run as a diluent or flush for the various reactants added in subsequent steps. In these four polymerizations, the weight ratio of total monomers charged was 85:15 styrene/butadiene.

The charges and the results of the runs are summarized in Table 16. Tapered butadiene/styrene blocks were formed in step 3 by charging both butadiene and styrene monomers. The charging sequence used was i, S₁, i, S₂, B₁/S₃, S₄, coupling agent. The monomer ratios corresponding to the S₁, S₂, B₁/S₃, S₄ sequence were 40, 20, 15/15, 10. Weight ratios of amounts of initiator used in the first two steps of each of the five runs was kept constant at 1:1.

The devolatilized copolymers from runs 3, 4, 5 and 6 were designated invention copolymers 3, 4, 5 and 6 had melt flows of 5.0 g/10 min, 9.4 g/10 min, 9.4 g/19 min and 7.4 g/10 min, respectively. The differences in melt flows were attributable to differences in amounts of initiator used in each of the four runs.

Injection molded test specimens of the block copolymers exhibited the properties shown in Table 18 after Example III.

TABLE 16

Invention Runs - Second Embodiment				
	Run 3	Run 4	Run 5	Run 6
<u>Step 1</u>				
Cyclohexane, phm	157	157	157	157
Tetrahydrofuran, phm	0.04	0.30	0.50	1.0
n-Butyllithium initiator, phm	0.03	0.03	0.03	0.03
Cyclohexane, phm	4.6	4.6	4.6	4.6
Styrene, phm	40	40	40	40
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	80.5	89.4	92.1	83.6
Peak Polymerization Pressure, psi	22	29	35	28
Polymerization Time, min	12	12	12	12
<u>Step 2</u>				
n-Butyllithium initiator, phm	0.06	0.055	0.05	0.04
Cyclohexane, phm	4.6			
Styrene, phm	20	20	20	20
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	81.3	84.8	88.3	86.7
Peak Polymerization Pressure, psi	30	34	28	37
Polymerization Time, min	11	11	11	11
<u>Step 3</u>				
Styrene, phm	15	15	15	15
Butadiene, phm	15	15	15	15
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	107.2	109.9	115.4	114.5
Peak Polymerization Pressure, psi	64	41	47	62
Polymerization Time, min	18	16	16	16
<u>Step 4</u>				
Styrene, phm	10	10	10	10
Cyclohexane, phm	4.6	4.6	4.6	4.6
Peak Polymerization Temperature, °C.	87.9	89.8	93.3	93.3
Peak Polymerization Pressure, psi	68	68	37	71
Polymerization Time, min	12	12	12	12
<u>Step 5 (Coupling)</u>				
Vikoflex ® 7170, phm	0.24	0.22	0.20	0.18
Cyclohexane, phm	4.6	4.6	4.6	4.6
Temperature, °C.	90	92	86	95
Pressure, psi	87	96	63	97

TABLE 16-continued

Invention Runs - Second Embodiment				
	Run 3	Run 4	Run 5	Run 6
<u>Step 6 (Terminating)</u>				
Water, phm	0.2	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4	0.4
Temperature, °C.	98	100	107	121
Pressure, psi	82	57	70	86
<u>Step 7 (Stabilizing)</u>				
Stabilizer Mixture, phm	1.25	1.25	1.25	1.25
Antiblocking agent, phm	0.3	0.3	0.3	0.3
<u>Recovered Resin</u>				
Melt Flow, g/10 min	5.0	9.4	9.4	7.4

Example III

Two more polymerization runs (7 and 8) were carried out according to the second embodiment of the invention to demonstrate the use of larger volumes of monomers. The procedure of Example I was followed with the exception that the sequence of charges shown in Table 17 was used. Again, the weight ratio of styrene to butadiene charged was 85 to 15. Samples were made with i, S₁, i, S₂, B₁/S₃, S₄ addition sequence followed by coupling; monomer ratios of 35, 20, 15/15, 15 were used.

In this example, 0.032 phm (run 7) initiator and 0.031 phm initiator (run 8) was charged in the first steps of the two runs. The amount of initiator charged in the second step was 0.075 phm (run 7) and 0.064 phm (run 8) for a range of ratios of amount of initiator in first step to amount in second step of 1:2.3 (run 7) to 1:2.1 (run 8).

Copolymers from runs 7 and 8, were devolatilized to form invention copolymers 7 and 8, which had melt flows of 8.1 g/10 min and 8.2 g/10 min, respectively. Injection molded test specimens of invention copolymers 7 and 8 exhibited the properties shown in Table 18.

TABLE 17

Invention Runs - Second Embodiment		
Components*	Run 7	Run 8
<u>Step 1</u>		
Cyclohexane, phm	168.9	168.9
Tetrahydrofuran	0.04	0.3
n-Butyllithium initiator, phm	0.032	0.031
Styrene, phm	35	35
Polymerization Time, min	4	2
Peak Polymerization Temperature, °C.	84.9	89.6
Peak Polymerization Pressure, psi	35.1	36.4
<u>Step 2</u>		
n-Butyllithium initiator, phm	0.075	0.064
Styrene, phm	20	20
Polymerization Time, min	3	3
Peak Polymerization Temperature, °C.	86.8	86.7
<u>Step 3</u>		
Butadiene, phm	15	15
Styrene, phm	15	15

TABLE 17-continued

Invention Runs - Second Embodiment		
Components ^a	Run 7	Run 8
Polymerization Time, min	8	6
Peak Polymerization Temperature, °C.	105.2	107.8
<u>Step 4</u>		
Styrene, phm	15	15
Polymerization Time, min	3	3
Peak Polymerization Temperature, °C.	88.0	88.9
<u>Step 5 (Coupling)</u>		
Vikoflex 7170, phm	0.28	0.25
Temperature, °C.	77.4	74.5
<u>Step 6 (Terminating)</u>		
Water, phm	0.2	0.2
Carbon Dioxide, phm	0.17	0.17
<u>Step 7 (Stabilizing)</u>		
Stabilizer Mixture, phm	1.25	1.25
BE Square wax	0.18	0.18
Recovered Resin		
Melt Flow, g/10 min	8.1	8.2

^aAfter each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5-20 phm cyclohexane diluent and cleared with nitrogen.

TABLE 18

Physical Properties of Injection Molded Articles Made from Invention Polymers (Second Embodiment)						
Property	Invention Polymer 3	Invention Polymer 4	Invention Polymer 5	Invention Polymer 6	Invention Polymer 7	Invention Polymer 8
Melt flow, g/10 min	5.0	9.4	9.4	7.4	8.1	8.2
Haze, %	1.0	0.7	1.1	1.4	1.0	0.9
Hunter blueness, b	-1.6	-3.1	-2.3	-2.1	-1.45	-1.63
Shore D Hardness	77	77	76	75	78	78
Notched Izod impact, 1/in	20.3	21.9	21.9	21.9	24.6	23.0
Tensile strength						
yield, MPa	43.4	39.1	38.5	33.5	39.0	37.5
break, MPa	30.3	24.1	24.9	22.9	26.4	25.9
Elongation						
yield, %	5.95	6.21	5.73	5.47	4.8	5.01
break, %	163	116	96	116	76.5	98.7
Flexural modulus, MPa	1565	1393	1407	1241	1662	1565

Example IV

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A polymerization was made to demonstrate the third embodiment of the invention. This run (9) was carried out according to the procedure of Example I with the exception that the sequences and amounts of charges shown in Table 19 were used. The weight ratio of styrene to butadiene charged was 85 to 15.

The coupled devolatilized copolymers from run 9 contained no tapered blocks, contained a single internal butadiene block (disregarding any coupling moiety) and had 65 terminal styrene blocks on each of the extending arms of each of the coupled polymeric species.

A copolymer from run 9 was devolatilized to form invention copolymer 9 which had a melt flow of 10.2 g/10 min.

TABLE 19

Invention Runs - Third Embodiment	
	Run 9
<u>Step 1</u>	
Cyclohexane, phm	168.9
Tetrahydrofuran, phm	0.04
n-Butyllithium initiator, phm	0.032
Styrene, phm	40
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	90.0
Peak Polymerization Pressure, psi	36.7
Polymerization Time, min	5
<u>Step 2</u>	
n-Butyllithium initiator, phm	0.034
Styrene, phm	20
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	87.7
Peak Polymerization Pressure, psi	34.4
Polymerization Time, min	4

TABLE 19-continued

Invention Runs - Third Embodiment	
	Run 9
<u>Step 3</u>	
n-Butyllithium initiator, phm	0.100
Styrene, phm	10
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	85.1

TABLE 19-continued

<u>Invention Runs - Third Embodiment</u>	
	Run 9
Peak Polymerization Pressure, psi	36.7
Polymerization Time, min	3
<u>Step 4</u>	
Styrene, phm	15
Cyclohexane, phm	1.1
Peak Polymerization Temperature, °C.	87.8
Peak Polymerization Pressure, psi	40.0
Polymerization time, min	3
<u>Step 5</u>	
Butadiene, phm	0.5
Cyclohexane, phm	1.1
Peak Polymerization Temperature, °C.	105.2
Peak Polymerization Pressure, psi	51.4
Polymerization time, min	5
Polymer Analysis (prior to coupling) (GPC area composition)*	
Peak 1	123.6
Peak 2	43.4
Peak 3	22.9
<u>Step 6 (Coupling)</u>	
Vikoflex 7170, phm	0.43
Cyclohexane, phm	0.6
Temperature, °C.	97.2
Pressure, psi	49.6
<u>Step 7 (Terminating)</u>	
Water, phm	0.2
Carbon Dioxide, phm	0.17
Temperature, °C.	—
Pressure, psi	—
<u>Step 8 (Stabilizing)</u>	
Stabilizer Mixture, phm	1.25
Antiblocking agent, phm	0.18
Recovered Resin	
Melt Flow, g/10 min	10.2

*Response of a dielectric detector in an Applied Automation process control GPC.

Injection molded test specimens of the polymodal block copolymer of run 9 were made and found to exhibit the properties shown in Table 20.

TABLE 20

<u>Physical Properties of Injection Molded Articles (Third Embodiment)</u>	
Property	Invention Polymer 9
Melt flow, g/10 min	10.2
Haze, %	0.7
Hunter blueness, b	-1.75
Shore D Hardness	77
Notched Izod impact, J/m	24.0
<u>Tensile strength</u>	
yield, MPa	47.9
break, MPa	48.3

TABLE 20-continued

<u>Physical Properties of Injection Molded Articles (Third Embodiment)</u>	
Property	Invention Polymer 9
<u>Elongation</u>	
yield, %	5.33
break, %	5.63
Flexural modulus, MPa	1972

Example V

A polymerization run was made for the purpose of demonstrating the fourth embodiment of this invention. The method of Example I was used, with the exception that the sequence and amounts of charges shown in Table 21 were used.

The polymodal block copolymer of run 10 (designated invention copolymer 10) had two sequentially internal tapered blocks and terminal styrene blocks on each of the coupled polymeric species. The block copolymer had a styrene to butadiene ratio of 88 to 12 and a melt flow of 20.0 g/10 min.

Injection molded test specimens of invention copolymer 10 exhibited the properties shown in Table 22.

TABLE 21

<u>Invention Run - Fourth Embodiment</u>	
	Run 10
<u>Step 1</u>	
Cyclohexane, phm	168.9
Tetrahydrofuran, phm	0.04
n-Butyllithium initiator, phm	0.022
Styrene, phm	40
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	84.0
Peak Polymerization Pressure, psi	34.6
Polymerization Time, min	5
<u>Step 2</u>	
n-Butyllithium initiator, phm	0.020
Styrene, phm	20
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	86.5
Peak Polymerization Pressure, psi	83.9
Polymerization Time, min	3
<u>Step 3</u>	
n-Butyllithium, initiator, phm	0.100
Styrene, phm	16
Cyclohexane, phm	1.7
Peak Polymerization Temperature, °C.	87.2
Peak Polymerization Pressure, psi	37.1
Polymerization Time, min	3
<u>Step 4</u>	
Butadiene, phm	5

TABLE 21-continued

<u>Invention Run - Fourth Embodiment</u>	
	Run 10
Styrene, phm	5
Cyclohexane, phm	2.2
Peak Polymerization Temperature, °C.	81.2
Peak Polymerization Pressure, psi	38.1
Polymerization Time, min	9
<u>Step 5</u>	
Butadiene, phm	7
Styrene, phm	7
Cyclohexane, phm	2.2
Peak Polymerization Temperature, °C.	87.3
Peak Polymerization Pressure, psi	43.8
Polymerization Time, min	7
Polymer Analysis (prior to coupling) (GPC area composition)*	
Peak 1	187.3
Peak 2	36.1
<u>Step 6 (Coupling)</u>	
Vikoflex 7170, phm	0.41
Cyclohexane, phm	0.6
Temperature, °C.	74.5
Pressure, psi	41.7
<u>Step 7 (Terminating)</u>	
Water, phm	0.2
Carbon Dioxide, phm	0.17
Temperature, °C.	—
Pressure, psi	—
<u>Step 8 (Stabilizing)</u>	
Stabilizer Mixture, phm	1.25
Antiblocking agent, phm	0.18
<u>Recovered Resin</u>	
Melt Flow, g/10 min	20.0

*Response of a dielectric detector in an Applied Automation process control GPC.

TABLE 22

<u>Physical Properties of Injection Molded Articles (Fourth Embodiment)</u>	
Property	Invention Polymer 10
Melt flow, g/10 min	20.0
Haze, %	0.8
Humer blueness, b	-1.7
Shore D Hardness	80
Notched Izod impact, J/m	20.8
<u>Tensile strength</u>	
yield, MPa	50.4
break, MPa	31.5
<u>Elongation</u>	
yield, %	6.37
break, %	15.71
Flexural modulus, MPa	1800

Example VI

Three more polymers were prepared to use in blends for comparison with the invention polymers. Polymerization

runs 11, 12 and 13 were carried out according to the method of Example II, except that the weight ratio of styrene to butadiene charged was 75 to 25 and samples were made with i, S₁, i, S₂, B₁/S₃, addition sequence followed by coupling; monomer ratios of 40, 10, 25/25 were used. The charges and results of the runs are shown in Table 23.

In each of the three runs of this example, 0.03 phm initiator was charged in the first step. The amount of initiator charged in the second step was varied from 0.08 phm (run 11) to 0.095 phm (run 13) for a range of ratios of amount of initiator in first step to amount in second step from 1:2.7 (run 11) to 1:3.2 (run 13).

Copolymers from runs 11, 12 and 13 were devolatilized to form comparative copolymers 11, 12 and 13, which had melt flows of 5.0 g/10 min, 5.4 g/10 min, and 7.1 g/10 min, respectively.

TABLE 23

<u>Comparative Runs</u>				
	Components*	Run 11	Run 12	Run 13
<u>Step 1</u>				
25	Cyclohexane, phm	145	145	145
	Tetrahydrofuran	0.04	0.04	0.04
	n-Butyllithium	0.03	0.03	0.03
	initiator, phm			
	Styrene, phm	40	40	40
	Polymerization Time, min	12	12	12
30	Peak Polymerization Temperature, °C.	77	79	76
<u>Step 2</u>				
	n-Butyllithium	0.08	0.085	0.095
	initiator, phm			
	Styrene, phm	10	10	10
35	Polymerization Time, min	12	12	12
	Peak Polymerization Temperature, °C.	64	71	65
<u>Step 3</u>				
	Butadiene, phm	25	25	25
40	Styrene, phm	25	25	25
	Polymerization Time, min	16	16	16
	Peak Polymerization Temperature, °C.	117	121	111
<u>Step 4 (Coupling)</u>				
45	Vikoflex 7170, phm	0.4	0.4	0.4
	Time, min	16	16	16
	Temperature, °C.	88	87	89
<u>Step 5 (Terminating)</u>				
	Water, phm	0.2	0.2	0.2
50	Carbon Dioxide, phm	0.4	0.4	0.4
	Time, min	25	25	25
	Temperature, °C.	82	82	84
<u>Step 6 (Stabilizing)</u>				
	Stabilizer Mixture, phm	1.25	1.25	1.25
55	BE Square wax	0.15	0.15	0.15
	Time, min	5	5	5
<u>Recovered Resin</u>				
	Melt Flow, g/10 min	5.0	5.4	7.1
	Mw/Mn, thousands	181/114	177/111	138/93
	Heterogeneity Index	1.6	1.6	1.69

*After each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5-20 phm cyclohexane diluent and cleared with nitrogen.

Example VII

Two more comparative polymers (14 and 15) were used for making comparisons of physical properties of blends of

the comparative polymers with polystyrene to physical properties of the invention copolymers.

Comparative polymer 14 was a resinous styrene-butadiene copolymer with a melt flow of 8.4 g/10 min. Polymer 14 was polymodal from multiple initiator and monomer charges (S, i, i, S, B, i, S, B) and coupled with an epoxidized vegetable oil coupling agent. Polymer 14 contained nominally 75 wt % styrene and 25 wt % butadiene with no styrene/butadiene tapered blocks. Comparative polymer 14 is similar to the third embodiment of the invention with the exceptions that comparative polymer 14 had a charge of butadiene in place of the third charge of initiator and monovinylarene monomer in the third embodiment and the third embodiment can have a proportionately higher monovinylarene content relative to conjugated diene content than comparative polymer 14 had. Polymer 14 formed 50:50 by weight blends with polystyrene that had high blueness and modest physical properties.

Comparative polymer 15 was a styrene-butadiene copolymer with no tapered block segments. Polymer 15 contained nominally 75 wt % styrene and 25 wt % butadiene and had a melt flow of 8.8 g/10 min. It had a polymodal molecular weight from multiple initiator and monomer charges (S, i, i, S, B) and was coupled with an epoxidized vegetable oil coupling agent. Comparative polymer 15 was similar to the third embodiment with the exceptions that: the third embodiment was made with two additional charges next preceding the conjugated diene charge, i.e., a charge of monovinylarene monomer and initiator followed by a charge of monovinylarene monomer; and, the third embodiment can contain a proportionately much larger monovinylarene content than that of comparative polymer 15. Polymer 15 formed 50:50 blends by weight with polystyrene that had low blueness and modest impact properties.

Example VIII

A series of blends of the comparison polymers from Examples VI and VII was prepared with Novacor® 555 general purpose polystyrene to demonstrate the properties of blends of the comparative copolymers containing total amounts of styrene similar to the total amounts of monovinylarene content in the invention copolymers of Examples I-V.

The blends were 50:50 or 60:40 styrene:butadiene by weight as indicated in the table and were prepared by solution blending in cyclohexane in a reactor at 100° C. with stirring for one hour. Each solution was flashed to remove the solvent and the polymer was dried, chopped in a granulator, and dried again. The dry polymer was processed on a roll mill and chopped again before injection molding on an Arburg model 90 injection molder with zones 1, 2, 3, and nozzle at 210° C., 210° C., 220° C., end 210° C., respectively, to make specimens to test for properties.

For convenient reference, blends are designated with the corresponding polymer numbers. For example, a blend prepared from comparative polymer 11 and polystyrene is comparative blend 11.

The results of tests of articles made from the comparative blends are shown in Table 24. Test specimens made from the blends of comparative polymers 11-15 exhibit significantly higher haze and blueness and significantly lower notched izod impact strengths than those of the inventive polymers. Thus the inventive polymers are superior to the blends in these areas for most applications. Also, the inventive polymers from embodiments 1 and 2 exhibit significantly higher tensile elongation at break than do the blend polymers,

indicating greater ductility. Generally, the other properties of the blends and inventive polymers are similar.

TABLE 24

Physical Properties of Test Specimens Made from Blends of Comparison Polymers with Polystyrene					
Property	Com- parative Blend 11	Com- parative Blend 12	Com- parative Blend 13	Com- parative Blend 14	Com- parative Blend 15
Blend ratio, S-B:PS*	50:50	50:50	50:50	50:50	50:50
Blend melt flow, g/10 min	30.2	10.7	12.8	16.8	17.5
Haze, %	8.1	3.4	4.2	4.3	2.7
Hunter	-16.2	-16.9	-17.1	-20.3	-16.8
blueness, b					
Shore D Hardness	77	77	77	77	79
Notched Izod impact, J/m	14.6	17.1	12.3	12.4	13.9
Vicat, °	82.9	92.1	92.0	85.3	89.3
Tensile strength					
yield, MPa	40.2	44.5	42.5	37.8	42.6
break, MPa	27.5	33.7	21.4	28.0	33.4
Elongation					
yield, %	5.3	6.2	6.2	4.8	4.8
break, %	18.2	14.7	13.7	32.0	15.77
Flexural modulus, MPa	1836	2091	2016	1979	2124

S-B:PS = Styrene-butadiene copolymer:polystyrene

Example IX

To provide comparison polymers having more than one tapered block, three more polymerization runs (16, 17 and 18) were carried out according to the procedures described in Example II, with the exception that the sequences and amounts of charges were as shown in Table 25. Tapered butadiene/styrene blocks were formed in the third and fourth steps by charging a mixture of butadiene and styrene monomers. The monomer addition sequence was i, S₁, i, S₂, B₁/S₃, B₂/S₄ followed by coupling; the monomer weight ratios were 40, 10, 12.5/12.5, 12.5/12.5, respectively. The polymers were 75 percent styrene and 25 percent butadiene.

In each of the three runs of this example the weight ratio of amount of initiator in the first step to the amount in the second step was kept constant at 1:1 with the absolute amount varied from 0.06 phm (run 16) to 0.055 phm (run 18).

The copolymers produced in the three runs were designated comparative copolymers 16, 17, and 18, and had melt flows of 14.3, 6.40 and 10.8 respectively. It is believed that lower melt flows are attributable to lower amounts of initiator. The polymerizations of invention runs 16, 17 and 18 are shown in Table 25.

TABLE 25

Comparative Runs			
Components*	Run 16	Run 17	Run 18
Step 1			
Cyclohexane, phm	145	145	145
Tetrahydrofuran, phm	0.04	0.04	0.04
n-Butyllithium	0.06	0.05	0.055
initiator, phm			
Styrene, phm	40	40	40

TABLE 25-continued

Comparative Runs			
Components ^a	Run 16	Run 17	Run 18
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	85	82	84
<u>Step 2</u>			
n-Butyllithium initiator, phm	0.06	0.05	0.055
Styrene, phm	10	10	10
Polymerization Time, min	12	12	12
Peak Polymerization Temperature, °C.	69	69	70
<u>Step 3</u>			
Butadiene, phm	12.5	12.5	12.5
Styrene, phm	12.5	12.5	12.5
Polymerization Time, min	16	16	16
Peak Polymerization Temperature, °C.	84	83	84
<u>Step 4</u>			
Butadiene, phm	12.5	12.5	12.5
Styrene, phm	12.5	12.5	12.5
Polymerization Time, min	16	16	16
Peak Polymerization Temperature, °C.	96	102	102
<u>Step 5 (Coupling)</u>			
Vikoflex 7170, phm	0.4	0.4	0.4
Time, min	16	16	16
Temperature, °C.	82	89	89
<u>Step 6 (Terminating)</u>			
Water, phm	0.2	0.2	0.2
Carbon Dioxide, phm	0.4	0.4	0.4
Time, min	25	25	25
Temperature, °C.	80	82	82
<u>Step 7 (Stabilizing)</u>			
Stabilizer Mixture, phm	1.25	1.25	1.25
Antiblocking agent, phm	0.15	0.15	0.15
Time, min	5	5	5
Temperature, °C.	80	n.a.	81
<u>Recovered Resin</u>			
Melt Flow, g/10 min	14.3	6.4	10.8
Mw/Mn, thousands	154/104	173/115	147/91
Heterogeneity Index	1.48	1.50	1.62

^aAfter each addition of monomer, initiator or additive, the feed lines were rinsed with approximately 5–20 phm cyclohexane diluent and cleared with nitrogen.

Example X

A series of blends of double tapered block comparative polymers with polystyrene was prepared for comparison of the properties of articles made from the blends to properties of invention polymers having two tapered blocks and similar total styrene content. Copolymers 16, 17, and 18 from Example IX were blended as described in Example VIII in 50:50 by weight mixtures with general purpose polystyrene to form comparative blends 16, 17, and 18. Test specimens were injection molded from the blends as described in Example VIII.

The results (Table 26) show that articles made from blends of comparative polymers 16, 17, and 18 had more modest Izod Impact values than those made from invention polymer 10 which also had two tapered blocks (shown in Table 22). Articles made from blends of the invention polymers also have less blueness than those made from comparative blends 16, 17 and 18.

TABLE 26

Physical Properties of Comparative Polymer Blends with Polystyrene ^a				
Property	Comparative Blend 16	Comparative Blend 17	Comparative Blend 18	Comparative Blend 14
Blend melt flow, g/10 min	14.8	12.0	14.8	16.8
Haze, %	4.1	4.0	5.1	4.3
Hunter blueness, b	-17.9	-18.5	-17.9	-20.3
Shore D hardness	76	77	76	77
Notched Izod impact, ft-lb	14.9	17.1	19.2	12.3
Vicat softening, °C.	89.3	90.5	90.5	85.3
<u>Tensile Strength</u>				
yield MPa	43.2	43.9	42.5	37.8
break MPa	28.6	28.7	28.7	28.0
<u>Elongation</u>				
yield, %	6.4	6.5	6.5	4.8
break, %	17.9	16.7	13.6	32.0
Flexural modulus, MPa	1988	1949	1986	1979
^a 50:50 Styrene-butadiene copolymer:polystyrene				

Example XI

Polymerization runs were carried out in a stirred, 100 gallon carbon steel reactor with internal cooling coils employing essentially anhydrous reactants and conditions.

Sequential polymerizations were conducted under nitrogen. Approximately 158 kg cyclohexane solvent (175 phm) were charged to the reactor. Reactants were charged to the reactor in the sequence and amount indicated in Table 27. Lines were flushed with 0.5 kg cyclohexane following each charge. Polymerization was allowed to continue to completion after each monomer or monomer mixture charge. Polymerization temperatures ranged from about 38° C. to about 110° C. and pressure ranged from about 2 psig to about 60 psig. Total monomer weight was about 90 kg.

After completion of sequential polymerizations, Vikoflex 7170, (a coupling agent comprising epoxidized soybean oil sold by Viking Chemical Co.) was charged to the reactor. After completion of the coupling reaction, the reaction was terminated by adding CO₂ and 0.2 phm water. The block copolymers were stabilized by adding 0.25 phm Irganox 1076 and 1.0 phm tris(nonylphenyl) phosphate to the reaction mixture.

The block copolymers and blends exhibited melt flows in the range of From 5 g/10 min. to 15 g/10 min. measured according to ASTM D-1238, condition G. The block copolymers and blends exhibited an Izod impact strength greater than 0.3 ft #/in. measured according to ASTM D-256. Blueness, tristimulus value "b", a measure of blue and yellow tint, was measured with a Hunter Lab Color Difference Meter 25 DM using three injection molded (350° F/30 tons/2 minutes) resin disks of 0.15 inch thickness and 2.5 inch diameter. Measurements were against a black background. A positive number represents yellow and a negative number represents blue.

Terms used in Table 27 are defined as follows:

S is styrene monomer in phm

i is n-butyllithium initiator in phm

B is 1,3-butadiene in phm

CA is epoxidized soybean oil coupling agent in phm

T is tetrahydrofuran in phm

Blend is 60 weight percent block copolymer (75S/25B) and 40 weight percent polystyrene

TABLE 27

Run	Blueness
Block Copolymer containing 88 weight % S	
101 0.04T, 40S, 0.03i, 0.02i, 20S, 5B/5S, 0.10i, 16S, 7B/7S, 0.41CA	-1.7
Block Copolymer containing 85 weight % S	
102 0.04T, 40S, 0.03i, 0.03i, 20S, 0.10i, 10S, 15S, 0.43CA	-1.8
103 0.04T, 40S, 0.03i, 0.03i, 20S, 0.10i, 10S, 15B/15S, 0.43CA	-2.4
104 0.3T, 40S, 0.03i, 0.02i, 20S, 0.04i, 10S, 15B/15S, 0.43CA	-4.3
Block Copolymer containing 70 weight % S	
105 0.04T, 37S, i, i, 19S, 9B, i, 14S, 21B, 0.41CA Blend containing 85 weight % S	-13.3
106 Block Copolymer/Polystyrene Blend	-11.7
107 Block Copolymer/Polystyrene Blend	-10.5
108 Block Copolymer/Polystyrene Blend	-15.6

The results in Table 27 indicate lower blueness values for inventive polymers in Runs 101-104, compared to similar block copolymers containing 70 weight % styrene or block copolymer/polystyrene blends containing 85 weight % styrene. The odor of styrene monomer was observed in the copolymer/polystyrene blends, Runs 106-108. The odor was not observed in Runs 101-105.

Example XII

Conjugated diene/monovinylarene Block Copolymers 1 and 2 were prepared by sequential solution polymerizations employing three initiator charges, three styrene charges, and at least one butadiene charge, where at least two styrene charges precede the butadiene charge. The temperature peaked at about 110° C. after each monomer charge and polymerization was allowed to continue to substantial completion. Following completion of the sequential polymerizations, Vikoflex 7170, (a coupling agent comprising epoxidized soybean oil solid by Viking Chemical Co.) was charged to the reactor. The sequence of addition and relative amount of each charge is outlined below. S is styrene, B is butadiene, i is n-butyllithium initiator, and CA is coupling agent.

Block Copolymer 2 and Polystyrene 555, available from Novacor Plastics Division, were blended to form Polymer Blend 3.

1. Block Copolymer containing 85 weight % S 40S, i, i, 15S, 5B/5S, i, 10S, 10B/15S, CA
2. Block Copolymer containing 75 weight % S 40S, i, i, 20S, 7.5B, i, 15S, 17.5B, CA
3. Polymer Blend Containing 85 weight % S in the final Blend 60 weight % Block Copolymer 2 40 weight % Polystyrene

Block Copolymer 1 and Polymer Blend 3, each containing 85 weight % styrene in the final composition, were tested for free styrene monomer and other residual organic compounds using gas chromatography. The results are tabulated in the table below. In Table 28, ppm is parts per million.

TABLE 28

	Block Copolymer 1	Polymer Blend 3
5	Toluene 1 ppm	2 ppm
	Vinylcyclohexene 3 ppm	1 ppm
	Ethylbenzene 0 ppm	1 ppm
	Isopropylbenzene 0 ppm	1 ppm
	n-Propylbenzene 0 ppm	0 ppm
10	Styrene Monomer 0 ppm	128 ppm

The data in Table 28, clearly indicate no free styrene monomer detected in Block Copolymer 1 containing 85 % styrene compared to 128 ppm free styrene monomer in Polymer Blend 3 also containing 85 % styrene. The results are consistent with the observations noted in Example XI.

While the polymers and methods of this invention have been described in detail for the purpose of illustration, the inventive polymers and methods are not to be construed as limited thereby. This patent is intended to cover all changes and modifications within the spirit and scope thereof.

That which is claimed is:

1. A method for preparing a block copolymer, said method comprising polymerizing under polymerization conditions by sequentially charging at least one monovinylarene monomer, an organomono alkali metal initiator, and at least one conjugated diene monomer, thereafter coupling with a polyfunctional coupling agent; and recovering said block copolymer;

wherein the step of polymerizing is conducted using a charge sequence of the following charges in the following order:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a mixture of monovinylarene monomer and conjugated diene monomer; and
- (d) a monovinylarene monomer;

wherein steps (a)-(b) are the only monomer and initiator charges used in the process;

wherein said at least one monovinylarene monomer contains from about 8 to about 18 carbon atoms and is provided in at least three monovinylarene charges; and wherein said at least one conjugated diene monomer contains from about 4 to about 12 carbon atoms and is provided in at least one conjugated diene monomer charge.

2. A method for preparing a block copolymer, said method comprising polymerizing under polymerization conditions by sequentially charging at least one monovinylarene monomer, an organoalkali metal initiator, and at least one conjugated diene monomer, thereafter coupling with a polyfunctional coupling agent; and recovering said block copolymer;

wherein the step of polymerizing is conducted using a charge sequence of the following charges in the following order:

- (a) a monovinylarene monomer and initiator;
- (b) initiator and a monovinylarene monomer;
- (c) a mixture of monovinylarene monomer and conjugated diene monomer;
- (d) a monovinylarene monomer and initiator; and
- (e) a mixture of monovinylarene monomer and conjugated diene monomer;

wherein steps (a)-(e) are the only monomer and initiator charges used in the process;

wherein said at least one monovinylarene monomer contains from about 8 to about 18 carbon atoms and is provided in at least three monovinylarene charges; and

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wherein said at least one conjugated diene monomer contains from about 4 to about 12 carbon atoms and is provided in at least one conjugated diene monomer charge.

3. A method according to claim 1 wherein said monomers are added in an amount in the range of about 55 to about 95 weight percent monovinylarene monomer and about 5 to about 45 weight percent conjugated diene monomer.

4. A method according to claim 3 wherein said monomers are added in an amount in the range of about 60 to about 95 weight percent monovinylarene monomer and about 5 to about 40 weight percent conjugated diene monomer.

5. A method according to claim 4 wherein said monomers are added in an amount in the range of about 80 to about 95 weight percent monovinylarene monomer and about 5 to about 20 weight percent conjugated diene monomer.

6. A method according to claim 1 wherein the first monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 30 weight percent to about 50 weight percent based on the total weight of the final block copolymer.

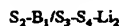
7. A method according to claim 6 wherein the second monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 15 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

8. A method according to claim 7 wherein the third monovinylarene monomer charge contains monovinylarene monomer in the range of from about 5 weight percent to about 30 weight percent based on the total weight of the final block copolymer.

9. A method according to claim 8 wherein said conjugated diene monomer is 1,3-butadiene and said monovinylarene monomer is styrene.

10. A monovinylarene/conjugated diene block copolymer consisting essentially

about 55 to about 95 weight percent polymerized monovinylarene based on total weight of said copolymer and about 5 to about 45 weight percent polymerized conjugated diene based on total weight of said copolymer; wherein said copolymer results from coupling block copolymer chains



wherein

S=monovinylarene block

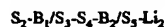
B/S=tapered block of conjugated diene/monovinylarene

Li=living polymer site or coupling site where subscripts 1 and 2 refer to the initiator charge sequence and said block copolymer chains are the only block copolymer chains present during the coupling.

11. A monovinylarene/conjugated diene block copolymer consisting essentially of;

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about 55 to about 95 weight percent polymerized monovinylarene based on total weight of said copolymer and about 5 to about 45 weight percent polymerized conjugated diene based on total weight of said copolymer; wherein said copolymer results from coupling block copolymer chains



wherein

S=monovinylarene block

B/S=tapered block of conjugated diene/monovinylarene

Li=living polymer site or coupling site where subscripts 1, 2 and 3 refer to the initiator charge sequence.

12. A method according to claim 2 wherein said monomers are added in an amount in the range of about 55 to about 95 weight percent monovinylarene monomer and about 5 to about 45 weight percent conjugated diene monomer.

13. A method according to claim 12 wherein said monomers are added in an amount in the range of about 60 to about 95 weight percent monovinylarene monomer and about 5 to about 40 weight percent conjugated diene monomer.

14. A method according to claim 13 wherein said monomers are added in an amount in the range of about 80 to about 95 weight percent monovinylarene monomer and about 5 to about 20 weight percent conjugated diene monomer.

15. A method according to claim 2 wherein the first monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 30 weight percent to about 50 weight percent based on the total weight of the final block polymer.

16. A method according to claim 15 wherein the second monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 15 weight percent to about 30 weight percent based on the total weight of the final block polymer.

17. A method according to claim 16 wherein the third monovinylarene monomer charge contains monovinylarene monomer in an amount in the range of from about 5 weight percent to about 30 weight percent based on the total weight of the final block polymer.

18. A method according to claim 17 wherein said conjugated diene monomer is 1,3-butadiene and said monovinylarene monomer is styrene.

* * * * *

United States Patent [19]

Fahrbach et al.

[11] 4,086,298

[45] Apr. 25, 1978

[54] BRANCHED BLOCK COPOLYMERS AND THEIR MANUFACTURE

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[52] U.S. Cl. 260/880 B

[58] Field of Search 260/880 B

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[57] ABSTRACT

Branched block copolymers of from 60 to 95 percent by weight of a monovinyl-aromatic compound and from 40 to 5 percent by weight of a conjugated diene. The copolymers have a structure of the general formula



where the A's are non-elastomeric polymer segments based on the monovinyl-aromatic compound, the B's are elastomeric polymer segments based on the conjugated diene, X is the radical of an at least trifunctional coupling agent and *n* and *m* are numbers. The copolymers may be used for the manufacture of highly transparent impact-resistant shaped articles, especially packaging materials.

10 Claims, No Drawings

BRANCHED BLOCK COPOLYMERS AND THEIR MANUFACTURE

The present invention relates to branched block copolymers which are built up of a predominant proportion of a monovinylaromatic compound and a lesser proportion of a conjugated diene, and which possess high transparency, high clarity and good mechanical properties, especially a high impact strength.

The manufacture, by polymerization of styrene and butadiene with lithium-hydrocarbons as initiators, of block copolymers in which one or more non-elastomeric polymer blocks are bonded to one or more elastomeric polymer blocks, has been disclosed. Depending on the content of the polymer blocks in the total polymer, these thermoplastic block copolymers exhibit non-elastomeric or elastomeric properties. Successive polymerization of the monomers results in block copolymers having a linear structure. If such linear block copolymers are coupled to one another by polyfunctional reactive compounds, branched block copolymers having a star-shaped structure result. Such branched block copolymers, described, for example, in British Pat. No. 985,614, have a symmetrical structure and in general exhibit better processability than the linear block copolymers.

It has also been disclosed that styrene-butadiene block copolymers having a high styrene content are clear thermoplastics having a high impact strength. Even though the block copolymers of this type, developed and proposed hitherto, have satisfactory properties in some respects, there are many practical requirements which they do not fulfil. In particular, their physical and mechanical properties leave something to be desired, or the products do not possess the transparency which is desirable for many applications.

German Laid-Open Application DOS 1,959,922 discloses branched copolymers having a star-shaped structure, obtained from a predominant proportion of styrene and a lesser proportion of a conjugated diene, which are stated to combine impact strength, clarity, good processability and resistance to external factors, in one and the same polymer. These branched block copolymers are obtained by coupling styrene-diene two-block copolymers in which the terminal polystyrene blocks have different lengths.

It is true that these products exhibit improved properties compared to the symmetrically branched block copolymers, but they do not prove fully satisfactory in respect of their mechanical properties, especially their impact strength, elongation at break and yield stress.

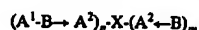
Unsymmetrical branched block copolymers are also described in German Laid-Open Application DOS 2,125,344. The advantage of these copolymers, which possess a homopolymer block in at least one branch, over symmetrical block copolymers is stated to be the lower solution viscosity of the polymers. In respect of their mechanical properties (impact strength), the polymers described in DOS 2,125,344, if based on a predominant proportion of styrene, are as unsatisfactory as the products known from DOS 1,959,922.

It is an object of the present invention to improve the mechanical properties of styrene-butadiene block copolymers which comprise a predominant proportion of styrene, and in particular to provide products having an increased impact strength and improved elongation at break. In addition, the products should be transparent

and as glass-clear as possible, and should possess good processability.

We have found that this object is achieved and that, surprisingly, non-elastomeric branched block copolymers of a monovinylaromatic compound and a conjugated diene possessing a quite specific block composition and structure in the branches, exhibit improved properties relative to comparable conventional block copolymers.

Accordingly, the present invention relates to branched block copolymers of from 60 to 95 percent by weight of a monovinyl-aromatic compound and from 40 to 5 percent by weight of a conjugated diene of 4 to 8 carbon atoms, which are built up of non-elastomeric polymer segments based on the monovinyl-aromatic compound and elastomeric polymer segments based on the conjugated diene and which are manufactured by anionic solution polymerization of the monomers by means of a monolithium-hydrocarbon as the initiator, followed by coupling of the resulting linear block copolymer with a polyfunctional coupling agent, wherein the average structure of the branched block copolymers corresponds to the general formula



where A^1 and A^2 are non-elastomeric polymer segments based on the monovinyl-aromatic compound and the B 's are elastomeric polymer segments based on the conjugated diene, n and m are numbers, m being equal to or greater than n and the sum of m and n being at least 3, and X is the radical of the polyfunctional coupling agent by means of which the polymer blocks, which form the branches, are chemically bonded to one another at the polymer segments A^2 , with the provisos that the polymer segment or segments A^1 contains or contain from 50 to 80 percent by weight of the total monovinyl-aromatic compound of the branched block copolymer, as copolymerized units, the transition between the polymer segments A^1 and B is sharp and the transition between the polymer segments B and A^2 is gradual.

Examples of monovinyl-aromatic compounds which can be used to synthesize the branched block copolymers of the invention are styrene, styrenes which are alkylated in the side chain, eg. α -methylstyrene and nuclear-substituted styrenes, eg. vinyltoluene or ethylvinylbenzene. The monovinyl-aromatic compounds may be employed individually or as mixtures with one another. Preferably, however, styrene alone is used. Examples of conjugated dienes which can be employed according to the invention, individually or as mixtures with one another, for the manufacture of the branched block copolymers, are butadiene, isoprene and 2,3-dimethylbutadiene. Butadiene and isoprene give particularly advantageous results, and of the two butadiene is preferred.

The branched block copolymers of the invention should in total contain from 60 to 95 percent by weight, especially from 70 to 90 percent by weight, of the monovinyl-aromatic compound and from 40 to 5 percent by weight, preferably from 30 to 10 percent by weight of the conjugated diene (in each case based on the total monomers employed), as copolymerized units. The molecular weight of the branched block copolymers is as a rule from 100,000 to 1,000,000 and preferably from 150,000 to 500,000. These figures relate to the

weight average molecular weight, determined by viscosity measurements in toluene at 25° C.

In detail, the branched block copolymers of the invention are manufactured by successive polymerization of the monomers in solution in the presence of a monolithium-hydrocarbon as the initiator, with stepwise addition of monomer and of initiator, followed by coupling of the resulting living linear block copolymers with a polyfunctional reactive compound as the coupling agent, as follows:

In a first process stage, the non-elastomeric polymer segment A¹ is produced by polymerizing a substantial portion of the total amount of the monovinyl-aromatic compound by means of a relatively small amount of the monolithium-hydrocarbon initiator in an inert solvent under conventional conditions. In this stage, from 50 to 80 percent by weight, preferably from 60 to 78 percent by weight, of the total amount of the monovinyl-aromatic compound employed, overall, for the manufacture of the branched block copolymers should be used. The total amount of monovinyl-aromatic compound used for the manufacture of the branched block copolymers is from 60 to 95 percent by weight, in particular from 70 to 90 percent by weight, based on the total monomers used for the manufacture of the polymer.

The amount of the initiator employed in the first stage of the process depends, above all, on the desired molecular weight of the polymer and is generally from 0.2 to 10 mmoles per mole of the monovinyl-aromatic compounds employed in the said first process stage. Preferably, from 0.4 to 2.5 mmoles of initiator per mole of the monovinyl-aromatic compounds employed in the first process stage are used in the said stage. The initiators employed are the conventional monolithium-hydrocarbons of the general formula RLi, where R is an aliphatic, cycloaliphatic, aromatic or mixed aliphatic-aromatic hydrocarbon radical, which may be of 1 to about 12 carbon atoms. Examples of the lithium-hydrocarbon initiators to be employed according to the invention are methyl-lithium, ethyl-lithium, n-, sec- and tert-butyl-lithium, isopropyl-lithium, cyclohexyl-lithium, phenyl-lithium and p-tolyl-lithium. The monolithium-alkyl compounds where alkyl is of 2 to 6 carbon atoms are preferred, n-butyl-lithium and sec-butyl-lithium being particularly preferred.

The polymerization of the monovinyl-aromatic compounds is carried out in solution in an inert organic hydrocarbon solvent. Suitable hydrocarbon solvents are aliphatic, cycloaliphatic and aromatic hydrocarbons which are liquid under the reaction conditions and are preferably of 4 to 12 carbon atoms. Examples are isobutane, n-pentane, isooctane, cyclopentane, cyclohexane, cycloheptane, benzene, toluene, the xylenes and others. Mixtures of these solvents may also be employed. Furthermore, the polymerization can be carried out in the presence of small amounts, in general from 10⁻³ to 5 percent by weight, based on total solvents, of ethers, eg. tetrahydrofuran, dimethoxyethane, phenyl methyl ether and others, whereby it is possible to influence, in the conventional manner, the rate of polymerization, the configuration of the butadiene polymer segment B and the statistical transition between the segments B and A². Preferably, however, no ether is added. The concentration of the monomers in the reaction solution is not critical and can be so chosen that any desired apparatus can be used for the polymerization. As a rule, the poly-

merization is carried out in from 10 to 30% strength solutions in the inert solvents.

The polymerization is carried out under the conventional conditions for anionic polymerizations with lithium-organic compounds, eg. in an inert gas atmosphere, with exclusion of air and moisture. The polymerization temperature may, for example, be from 0° to 120° C and is preferably kept at from 40° to 80° C.

In this first stage of the process, the polymerization is taken to virtually complete conversion of the monovinylaromatic compounds employed. This gives a solution of non-elastomeric, living linear polymers of the monovinyl-aromatic compounds (polymer segment A¹) with active terminal lithium-carbon bonds capable of further addition of monomers.

In the second stage of the process, the polymer segments B, followed by the polymer segments A², are polymerized onto the living active chain ends of these polymer segments A¹, to form the polymer block (A¹-B-A²) of the branched structure, and at the same time, in the same reactor, the copolymer blocks (B-A²) of the branched structure are formed. For this purpose, a further amount of initiator and a mixture of the remaining monovinyl-aromatic compound and the conjugated diene are added to the fully polymerized reaction solution from the first stage of the process, and polymerization is carried out. The amount of conjugated diene is from 5 to 40 percent by weight, preferably from 10 to 30 percent by weight, of the total monomers employed for the manufacture of the branched block copolymers of the invention. The amount of fresh initiator which is added to the reaction solution in the second stage of the process should be as great or greater, than the original amount of initiator which has been employed in the first stage of the polymerization process. Preferably, the amount of fresh initiator added in the second stage of the process is from 1 to 15 times, and in particular from 1 to 10 times, the amount of initiator added originally. It is particularly advantageous to add from 1 to 5 times the amount, especially when, as explained in more detail below, trifunctional or tetrafunctional coupling agents are employed in the subsequent coupling reaction. Suitable initiators are the monolithium-hydrocarbons, which can also be employed in the first stage of the process; preferably, the initiator used is identical to that used in the first stage of the process. It is advantageous to add the fresh initiator to the reaction solution before the monomer mixture of the remaining monovinyl-aromatic compound and the conjugated diene is added.

In the second process stage, the same polymerization conditions may be maintained as in the first stage, and here again polymerization is taken to virtually complete conversion of the monomers. In this polymerization, the monomers added in the second stage of the process are added onto the active living chain ends of the previously formed monomer segments A¹, but new chains of living polymers are also formed by the fresh initiator added. Because of the different copolymerization parameters, the conjugated dienes polymerize substantially more rapidly than the monovinyl-aromatic compounds, so that after addition of the monomer mixture in the second stage of the process, it is first predominantly the conjugated dienes which undergo polymerization, and only occasional polymerized units of the monovinyl-aromatic compounds are formed. Only toward the end of the diene polymerization, ie. when almost all the conjugated diene has polymerized, does

the polymerization of the monovinyl-aromatic compounds commence to a significant degree, so that the predominant proportion — as a rule more than 70 percent by weight, and in most cases up to 80 percent by weight — of the monovinyl-aromatic compounds contained in the monomer mixture only polymerizes after the conjugated diene has been consumed.

Accordingly, in the second stage of the process an elastomeric polymer segment B, based on the conjugated dienes, is first formed, this being a copolymer of a predominant proportion of the conjugation diene with small amounts of the monovinyl-aromatic compound; after which a non-elastomeric polymer segment A² is formed, which is made up of the monovinyl-aromatic compounds only. Since the proportion of the monovinyl-aromatic compounds progressively increases toward the end of the polymer segment B and the proportion of the conjugated diene correspondingly decreases, the transition between the polymer segments B and A² formed is not sharp and instead occurs gradually; this is therefore frequently described as a blurred transition between the segments. This fact is taken into account, in the general formula for the branched block copolymers of the invention, by the use of the symbol →.

After complete polymerization of the monomer mixture in the second stage of the process, the reaction solution thus contains a mixture of living linear block copolymers of the type (A¹→B→A²)—Li and (B→A²)—Li, each with reactive lithium-carbon bonds at the free end of the polymer segments A². The ratio of the two types of block copolymers in the reaction solution corresponds to the ratio of the amounts of initiator in the first and second stages of the process.

The mixture of these two types of active living linear block copolymers is then reacted in a further stage of the process, in which is added a polyfunctional reactive compound to act as the coupling agent. The polyfunctional coupling agent used should be at least trifunctional, i.e. it should be capable of reacting with three or more of the active living block copolymer chains, at the terminal lithium-carbon bonds of these, to form a chemical bond, so that a single coupled and accordingly branched block copolymer is formed. The coupling of lithium-terminated living polymers with polyfunctional coupling agents is known in the art and disclosed, for example, in the publications cited initially, especially British Pat. No. 985,614.

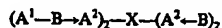
Examples of suitable coupling agents for the manufacture of the branched block copolymers of the invention are polyepoxides, eg. epoxidized linseed oil, polyisocyanates, eg. benzo-1,2,4-trisocyanate, polyketones, eg. 1,3,6-hexanetrione or 1,4,9,10-anthracenetetrone, polyanhydrides, eg. the dianhydride of pyromellitic acid, or polyhalides. Dicarboxylic acid esters, eg. diethyl adipate or the like, can equally be used as coupling agents. A further preferred group of coupling agents comprises the silicon halides, especially silicon tetrachloride, silicon tetrabromide, trichloroethylsilane or 1,2-bis(methyldichlorosilyl)-ethane. Further coupling agents which can be employed are polyvinyl-aromatics, especially divinylbenzene, as described, eg., in U.S. Pat. No. 3,280,084. In this case, some divinylbenzene units add on, producing crosslinking and forming a branching center, through which the preformed polymer blocks are bonded to one another.

The nature of the polyfunctional coupling agent used is not critical provided it does not significantly detract

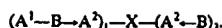
from the desired properties of the end product. The use of a trifunctional or tetrafunctional coupling agent of the above type, or of divinylbenzene, is preferred. In general, the polyfunctional coupling agent is added to the reaction solution in amounts equivalent to the total amount of the "living" polymer blocks, i.e. equivalent to the number of active lithium-carbon bonds in the preformed linear block copolymers. The reaction of the living linear block copolymers with the coupling agent is preferably carried out under the same reaction conditions as the preceding polymerization of the monomers. The resulting branched block copolymers are isolated from the reaction solution by conventional methods, eg. by precipitating the polymer from the reaction solution, and filtering it off.

If desired, the branched block copolymer can be hydrogenated following the coupling reaction and, advantageously, before isolating the product from the reaction solution. The hydrogenation may be carried out selectively or non-selectively and is normally effected with the aid of molecular hydrogen and catalysts based on metals, or salts of metals, of group 8 of the periodic table. The hydrogenation can be carried out in a homogeneous phase with catalysts based on salts, especially the carboxylates, alkoxides or enolates of cobalt, nickel or iron, which have been reduced with metal alkyls, especially aluminum alkyls, as disclosed, for example, in U.S. Pat. No. 3,113,986, German Published Application DAS 1,222,260 or German Laid-Open Application DOS 2,013,263. In these reactions, the olefinic double bonds are hydrogenated under mild conditions at hydrogen pressures of from 1 to 100 bars, and at from 25° to 150° C. The hydrogenation can also be carried out in a heterogeneous phase, with metallic nickel or metals of the platinum group as catalysts, at hydrogen pressures of from 20 to 300 bars and at from 40 to 300 bars and at from 40° to 300° C (for example, by the method of German Published Application DAS 1,106,961 or German Laid-Open Application DOS 1,595,345). In this reaction, not only the olefinic double bonds but also the aromatic double bonds are hydrogenated. If the hydrogenation is carried out in solution, it is advantageously effected in the same solvent as the preceding polymerization. The branched block copolymer may be hydrogenated partially or completely. If a hydrogenation is carried out, it is preferred selectively to hydrogenate the olefinic double bonds of the polymer, so that the hydrogenated branched copolymers obtained preferably only contain less than 10% and especially less than 3%, of olefinic double bonds. The hydrogenation is preferably carried out on branched block copolymers which have been manufactured in the presence of small amounts of ethers during the polymerization.

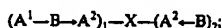
The process of manufacture decides the composition and structure of the branched block copolymers of the invention. If, for example, a tetrafunctional coupling agent is used and the ratio, in the fully polymerized reaction solution from the second stage of the process, of the two types of block copolymers which form the branches, namely the ratio of (A¹→B→A²)—Li to (B→A²)—Li, is, for example, 1:1 or 1:3, the resulting branched block copolymer will on average (most probable structure) possess a structure of the formula



or

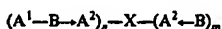


In the case of a trifunctional coupling agent and a ratio of the two types of branches, namely $(A^1-B-A^2)-Li$ to $(B-A^2)-Li$, of 1:2, the most probable average structure of the branched block copolymer is



in each of the formulae, X is the radical of the coupling agent.

In general, the most probable average structure of the branched block copolymers manufactured according to the invention corresponds to the general formula



where m and n are integers, and the sum of n and m is equal to the polyfunctionality of the coupling component and is thus at least 3, in general from 3 to 10 and preferably 3 or 4. m is equal to or greater than n . The non-elastomeric polymer segment A^1 , which contains from 50 to 80 percent by weight, preferably from 60 to 78 percent by weight, of the total monovinyl-aromatic compound, employed for the manufacture of the branched block copolymer, as polymerized units, preferably consists only of the monovinylaromatic compounds and is thus in particular a homopolystyrene segment. Its molecular weight depends particularly on the envisaged end use of the final product and is preferably from 50,000 to 250,000. As stated, the elastomeric polymer segment B is a copolymer block consisting essentially of the conjugated diene with a small proportion of monovinyl-aromatic compound, and in particular the olefinic double bonds can be selectively hydrogenated. The proportion of monovinyl-aromatic compound in the polymer segment B is in general less than about 30 percent by weight and in particular less than about 20 percent by weight, based on the amount of vinyl-aromatic not contained in the polymer segment A^1 . The non-elastomeric polymer segments A^2 , line the polymer segment A^1 , preferably are built up of the monovinyl-aromatic compound alone, and in particular are homopolystyrene. The molecular weight of the polymer blocks $(B-A^2)$ is preferably from 10,000 to 100,000.

The branched block copolymers of the invention possess high transparency and clarity and good mechanical properties, and in particular are superior, in respect of impact strength and elongation at break, to the conventional products described in German Laid-Open Application DOS 1,959,922. This was not foreseeable, and was all the more surprising since, according to the teaching of DOS 1,959,922, all non-elastomeric polymer segments must be in terminal positions if satisfactory mechanical properties are to be achieved. Hydrogenation can in particular improve the aging resistance of the products, though it may result in some reduction in their transparency. The branched block copolymers of the invention can easily be processed by the conventional processing methods for thermoplastics, eg. extrusion, deep-drawing or injection molding, and may be used, for example, for the manufacture of packaging.

The Examples which follow illustrate the invention. The viscosity number, measured in 0.5% strength solution in toluene at 25° C, is quoted as a measure of the

molecular weight. The impact strength a_k and notched impact strength a_k were determined on a molded specimen according to DIN 53,453. The yield stress Y, tensile strength Z and elongation at break D were measured on a compression-molded dumbbell-shaped bar according to DIN 53,455.

EXAMPLE 1

2 kg of toluene and 250 g of styrene were titrated with n-butyl-lithium, in a 6 l pressure kettle under an inert gas atmosphere, with exclusion of moisture, until polymerization commenced. 2.25 mmoles of n-butyl-lithium (as a solution in n-hexane) were then added and the mixture was polymerized at 50° C for about 1.5 hours, until the styrene was virtually completely converted. The resulting polystyrene segments had a viscosity number of 47.2 (cm³/g). A further 6.75 mmoles of n-butyl-lithium (as a solution in n-hexane) were added to the solution of polystyryl-lithium, and a mixture of 125 g of styrene and 125 g of butadiene was then added to the reaction solution. The temperature was kept at from 50° to 55° C. After about 3 hours, polymerization was virtually complete. 2.25 mmoles of silicon tetrachloride were then added as the coupling agent and the reaction solution was kept for 15 hours at room temperature. The polymer was then precipitated from the solution by adding methanol, filtered off and dried.

The branched block copolymer obtained had an average approximate structure of [polystyrene-poly(butadiene/styrene)-polystyrene]₁-Si-[polystyrene-poly(butadiene/styrene)]₂ and a viscosity number of 76.8 (cm³/g). Its mechanical properties are shown in the table below.

EXAMPLE 2

The procedure followed was as described in Example 1, but in this case 2.4 kg of toluene and 350 g of styrene were initially introduced into the reactor. After titrating the reaction solution with n-butyl-lithium, 4.66 mmoles of n-butyl-lithium were added to initiate the polymerization, which was carried out at 50° C until the styrene was completely converted. The resulting polystyrene had a viscosity number of 37.1 (cm³/g). A further 4.66 mmoles of n-butyl-lithium were then added, followed by a mixture of 106 g of styrene and 170 g of butadiene. After completion of the polymerization, coupling was carried out with 23.3 mmoles of silicon tetrachloride. The viscosity number of the end product was 99.9 (cm³/g). The approximate structure of the branched block copolymer was [polystyrene-poly(butadiene/styrene)-polystyrene]₁-Si-[polystyrene-poly(butadiene/styrene)]₂. The mechanical properties are summarized in the table.

COMPARATIVE EXAMPLE (according to German Laid-Open Application DOS 1,959,922)

2.7 kg of cyclohexane and 600 g of styrene were titrated with sec.-butyl-lithium in a 6 l pressure kettle under an inert gas atmosphere and then polymerized for 30 minutes with 0.33 g of sec.-butyl-lithium. The initial temperature was 54° C. 0.22 kg of cyclohexane, 0.9 g of sec.-butyl-lithium and 225 g of styrene were added to the reaction solution at 71° C, polymerization was carried out for one hour, and 250 g of butadiene were then polymerized onto the product in the course of 1 hour at about 74° C. Finally, coupling was carried out with 10 ml of Epoxyl 9-5 in 150 ml of toluene. The product was

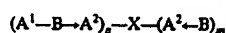
precipitated from isopropanol. The viscosity number was 91.9 (cm³/g).

TABLE

	a_n (cm . kg/ cm ²)	a_k (cm . kg/ cm ²)	Y (kp/cm ²)	Z (kp/cm ²)	D (%)
Example 1	33.5	16.8	290	175	410
Example 2	30% fracture	2.5	214	269	431
Comparative Example	15.1	5.4	170	190	91

We claim:

1. Branched block copolymers of from 60 to 95 percent by weight of a monovinyl-aromatic compound and from 40 to 5 percent by weight of a conjugated diene of 4 to 8 carbon atoms, which have an average structure of the general formula



where A¹ and A² are non-elastomeric polymer segments based on the monovinyl-aromatic compound and the B's are elastomeric polymer segments based on the conjugated diene, *n* and *m* are numbers, *m* being equal to or greater than *n* and the sum of *m* and *n* being at least 3, and X is the radical of the polyfunctional coupling agent by means of which the linear polymer blocks (A¹-B-A²) and (B-A²), which form the branches, are chemically bonded to one another at the polymer segments A², with the provisos that the polymer segment or segments A¹ contains or contain from 50 to 80 percent by weight of the total monovinyl-aromatic compound of the branched block copolymer, as copolymerized units, the transition between the polymer segments A¹ and B is sharp and the transition between the polymer segments B and A² is gradual.

2. Branched block copolymers as set forth in claim 1, which have a weight-average molecular weight of from 100,000 to 1,000,000.

3. Branched block copolymers as set forth in claim 1, which are partially or completely hydrogenated.

4. A process for the manufacture of branched block copolymers of claim 1 which comprises: polymerizing in a first stage of the process, from 50 to 80 percent by weight of the total amount of monovinyl-aromatic compound in an inert solvent, in the presence of a relatively small amount of a monolithium-hydrocarbon as the initiator until conversion is virtually complete, thereafter, in a second stage of the process, adding to the reaction solution a further amount of monolithium-hydrocarbon, which is equal to or greater than the amount of initiator originally employed, followed by the addition of a mixture of the remaining monovinyl-aromatic compound and the conjugated diene, and again carrying out the polymerization until the monomers have been virtually completely converted, thereafter subjecting the mixture of the resulting linear block copolymers with active terminal lithium-carbon bonds to a coupling reaction, by adding a polyfunctional coupling agent, to form a branched block copolymer and finally isolating the branched block copolymer from the reaction solution.

5. A branched block copolymer as set forth in claim 1, wherein the monovinyl-aromatic compound is styrene, styrene alkylated in the side chain and nuclear substituted styrene.

6. A branched block copolymer as set forth in claim 1, wherein the conjugated diene is butadiene, isoprene and 2,3-dimethylbutadiene.

7. A branched block copolymer as set forth in claim 1, wherein the polyfunctional coupling agent is a polyepoxide, polyisocyanate, polyketone, polyanhydride, polyhalide, dicarboxylic acid ester, silicon halide or polyvinyl-aromatic.

8. A branched block copolymer as set forth in claim 1, wherein the sum of *n* + *m* is from 3 to 10.

9. A process as set forth in claim 4, wherein the amount of initiator in the first stage is from 0.2 to 10 moles per mole of the monovinyl-aromatic compound.

10. A process as set forth in claim 4, wherein the amount of initiator in the second stage is from 1 to 15 times the amount of initiator added in the first stage.

* * * * *



US005854353A

United States Patent [19]

Knoll et al.

[11] **Patent Number:** **5,854,353**[45] **Date of Patent:** **Dec. 29, 1998**[54] **THERMOPLASTIC MOLDING COMPOUND**[75] **Inventors:** **Konrad Knoll**, Ludwigshafen;
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of Germany[73] **Assignee:** **BASF Aktiengesellschaft**,
Ludwigshafen, Germany[21] **Appl. No.:** **750,635**[22] **PCT Filed:** **May 31, 1995**[86] **PCT No.:** **PCT/EP95/02072**§ 371 Date: **Dec. 16, 1996**§ 102(c) Date: **Dec. 16, 1996**[87] **PCT Pub. No.:** **WO95/34586****PCT Pub. Date:** **Dec. 21, 1995**[30] **Foreign Application Priority Data**

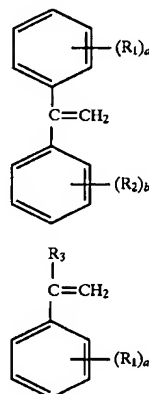
Jun. 16, 1994	[DE]	Germany	44 20 917.7
Oct. 13, 1994	[DE]	Germany	44 36 499.7

[51] **Int. Cl.⁶** **C08F 293/00**[52] **U.S. Cl.** **525/314; 526/346; 526/347**[58] **Field of Search** **525/314; 526/346,**
526/347[56] **References Cited****U.S. PATENT DOCUMENTS**

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WPI Derwent Abstracts, AN 91-143958[20] (English
abstract of JP-3079613, Aug. 22, 1989).*Primary Examiner*—Edward J. Cain
Attorney, Agent, or Firm—Kcil & Weinkauff[57] **ABSTRACT**Thermoplastic molding compounds comprise as essential
componentsA) from 10 to 100% by weight of copolymers of the
monomers of the general formulae I and II

where

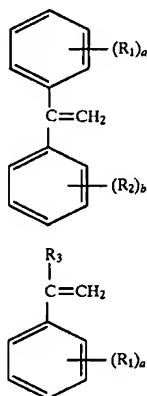
 R_1 is H or alkyl of 1-22 carbon atoms, R_2 is H or alkyl of 1-22 carbon atoms, R_3 is H or alkyl of 1-4 carbon atoms, a is 0, 1, 2, 3, 4 or 5, and b is 0, 1, 2, 3, 4 or 5,B) from 0 to 3000 ppm, based on the weight of component
A, of compounds of the general formula I,C) from 0 to 500 ppm, based on the weight of component
A, of compounds of the general formula II,D) from 0 to 90% by weight, based on the total weight of
the molding compound, of polymers other than A), andE) from 0 to 50% by weight, based on the total weight of
the molding compound, of additives and processing
aids.**8 Claims, No Drawings**

THERMOPLASTIC MOLDING COMPOUND

DESCRIPTION

The present invention relates to thermoplastic molding compounds comprising as essential components

A) from 10 to 100% by weight of copolymers of the monomers of the general formulae I and II



where

R_1 is H or alkyl of 1-22 carbon atoms,

R_2 is H or alkyl of 1-22 carbon atoms,

R_3 is H or alkyl of 1-4 carbon atoms,

a is 0, 1, 2, 3, 4 or 5, and

b is 0, 1, 2, 3, 4 or 5,

B) from 0 to 3000 ppm, based on the weight of component A, of compounds of the general formula I,

C) from 0 to 500 ppm, based on the weight of component A, of compounds of the general formula II,

D) from 0 to 90% by weight, based on the total weight of the molding compound, of polymers other than A), and

E) from 0 to 50% by weight, based on the total weight of the molding compound, of additives and processing aids.

Molded thermoplastics are hard and rigid at room temperature. At higher temperatures, however, the usefulness of thermoplastics is limited by the glass transition temperature or by the melting point in the case of partly crystalline thermoplastics. This also applies to atactic polystyrene, whose glass transition temperature is 101° C. and which does not crystallize because of the irregular orientation of the phenyl rings. Lately it has been possible, by means of metallocene catalysis, to produce a syndiotactic polystyrene whose crystalline regions have a melting point of 275° C. (e.g. EP-A-210 615, EP-A-535 582, EP-A-312 976 and EP-A-318 833).

Syndiotactic polystyrene, however, has various disadvantages. For instance, the processing range for the production of moldings is relatively small, since the product has to be heated to above the melting point on the one hand, but it will decompose at above 310° C. on the other. The consequence is that the product readily depolymerizes back to styrene monomer during processing.

Furthermore, the product crystallizes in various forms which have a significant effect on the performance characteristics of the molded part. Finally, only the crystalline regions have the high melting point; the amorphous regions still have a glass transition temperature of 101° C. as before.

The polymerization of 1,1-diphenylethylene with styrene is known and described in Bulletin Chem. Soc. Jap. 40

(1967), 2569, and in J. Polymer Sci., Part B, 8 (1970), 499. However, the method described in these publications has the disadvantage that the polymerization proceeds extremely slowly and the conversion is incomplete if higher softening points are to be obtained.

The diphenylethylene monomer remaining in the copolymer lowers its glass transition temperature and so makes it worthless for commercial purposes.

It is an object of the present invention to provide thermoplastic molding compounds which are free of the above-described disadvantages, which have a glass transition temperature of at least 130° C. and which have a residual monomer content of <4000 ppm.

We have found that this object is achieved by thermoplastic molding compounds as claimed in claim 1.

Preferred molding compounds of this invention are disclosed in the subclaims.

Component A of the thermoplastic molding compounds of this invention comprises from 10 to 100, preferably from 40 to 100, especially from 60 to 100, % by weight, based on the proportion of polymeric components, of a copolymer having units derived from monomers I and II.

The monomers of the general formula I are 1,1-diphenylethylene and its derivatives where the aromatic rings are substituted by alkyl having up to 22 carbon atoms.

Preferred alkyl substituents are alkyl groups having 1 to 4 carbon atoms, such as methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl and tert-butyl, to name but a few. However, the unsubstituted 1,1-diphenylethylene itself is particularly preferred.

The monomers of the general formula II are styrene and its derivatives where there is substitution by alkyl having 1 to 4 carbon atoms in the α -position or on the aromatic ring. Preferred alkyl groups are those mentioned above as preferred for monomers of the formula I; unsubstituted styrene itself is particularly preferred.

The molar ratio of units derived from monomer I to units derived from monomer II is generally within the range from 1:1 to 1:25, preferably within the range from 1:1.05 to 1:15, particularly preferably within the range from 1:1.1 to 1:10. Since the monomers of the formula I generally do not homopolymerize, products having molar ratios of more than 1:1 are not readily obtainable.

The novel process for producing component A) of the molding compounds of this invention comprises providing the monomers of the formula I as initial charge and metering in the monomers of the formula II during the reaction according to a gradient method such that, as the reaction progresses, the amount of monomer II added per unit time is essentially reduced according to the amount of monomer I still present. This manner of performing the reaction keeps the monomer ratio approximately constant during the entire polymerization. To control the addition gradient, it is advantageously possible to utilize the change in the refractive index, which is a function of the monomer ratio. A further possibility is to determine the monomer ratio as a function of the conversion in a number of preliminary experiments and so to obtain an appropriate calibration curve.

The monomers mentioned are advantageously reacted in an inert solvent. "Inert" in this context means that the solvent does not react with the organometallic initiator customarily used for initiating the reaction. Both aliphatic and aromatic hydrocarbons are therefore suitable in general. Examples of suitable solvents include cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene and xylene.

Finally, it is also possible to use hydrocarbons in which the copolymer formed in the course of the reaction is not

soluble. In this case, a precipitation polymerization or, by means of a dispersant, a dispersion polymerization can be carried out instead of the solution polymerization. Examples of suitable reaction media for such process variants include butane, pentane, n-hexane, isopentane, heptane, octane and isooctane.

The polymerization is generally initiated by means of organometallic compounds; i.e., the polymerization is an anionic polymerization. Preference is given to compounds of the alkali metals, especially of lithium. Examples of initiators are methyl lithium, ethyllithium, propyllithium, n-butyllithium, sec-butyllithium and tert-butyllithium. The organometallic compound is generally added as a solution in a chemically inert hydrocarbon. The rate of addition depends on the molecular weight desired for the polymer, but is generally within the range from 0.002 to 5 mol %, on the basis of the monomers.

Small amounts of polar aprotic solvents can be added to obtain higher polymerization rates. Examples of suitable solvents are diethyl ether, diisopropyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether and, especially, tetrahydrofuran. The polar cosolvent is generally added to the apolar solvent in a small amount of about 0.5–5% by volume in this process variant. Particular preference is given to THF in an amount of 0.1–0.3% by volume. Pure THF has an adverse influence on the reaction parameters, so that the polymer comprises high residual levels of monomers of the formula I.

The polymerization temperature can be within the range from 0° to 130° C. Preference is given to temperatures of 50°–90° C. In general, the polymerization is carried out under isothermal conditions; that is, with a constant polymerization temperature. However, the temperature can also be allowed to rise within the range of 0°–130° C., preferably 30°–120° C. It is particularly advantageous to carry out the initial part of the polymerization under isothermal conditions and to allow the temperature to rise adiabatically toward the end of the polymerization, i.e. at low monomer concentrations, in order that the polymerization times may be kept short.

The reaction times are generally within the range from 0.1 to 24, preferably from 0.5 to 12, particularly preferably from 1 to 10, h.

Component B) of the thermoplastic molding compounds of this invention comprises from 0 to 3000, preferably from 0 to 2000, particularly preferably from 100 to 1000, ppm of monomers of the formula I. Preferably, the monomers have the same formula as the monomers incorporated into the copolymer in the course of the polymerization.

Component C) of the thermoplastic molding compounds of this invention comprises from 0 to 500, preferably from 0 to 200, in particular from 20 to 100, ppm of monomers of the formula II. These monomers preferably have the same chemical formula as the monomers used in preparing component A).

The amounts of components B) and C) are based on the weight of component A in the thermoplastic molding compounds.

Component D) of the thermoplastic molding compounds of this invention comprises from 0 to 90, preferably up to 60, especially up to 30, % by weight, based on the total weight of the molding compound, of further components other than copolymer A). In principle, no particular restriction applies as to the structure of these further polymeric components; however, preference is given to polymers which have at least a certain degree of compatibility with component A), since the mechanical properties are generally not satisfactory

otherwise. Preferred polymers are styrene polymers such as high impact or crystal polystyrene or else polyphenylene ether addition polymers with or without an admixture of styrene polymers.

Furthermore, the thermoplastic molding compounds of this invention may additionally include as component E) up to 50% by weight, based on the total weight of the thermoplastic molding compound, of further, additive substances and processing aids. Such additives are known to the person skilled in the art and described in the literature, so that there is no need for details here. Examples are fibrous and particulate fillers, stabilizers against heat and UV light, demolding agents and lubricants. Similarly, pigmentation of the molding compounds of this invention is possible, of course.

A further embodiment of the present invention takes the form of block copolymers with blocks A and B of the following general structures: $(A-B)_n$, $A-B-A$, $B-A-B$, $X[(A-B)_n]_m$, $X[(B-A)_n]_m$, $X(A-B-A)_m$, or $X(B-A-B)_m$ where A is a block of a copolymer of monomers of the general formulae I and II, B is a block of monomers of the general formula II, X is the radical of an m-functional coupling agent, n is an integer from 1 to 5, and m is an integer from 2 to 20.

The coupling agent X reacts with the living anionic chain ends after the polymerization to form the above-described structures. Examples of suitable coupling agents may be found in U.S. Pat. Nos. 3,985,830, 3,280,084, 3,637,554 and 4,091,053. Merely illustrative examples are epoxidized glycerides such as epoxidized linseed oil or soybean oil; divinylbenzene is also suitable. If the living anionic end is situated on the B-block, then the coupling is preferably carried out with compounds containing epoxy and/or ester groups; if, however, the A-block forms the active end, it is preferable to use divinylbenzene for the coupling.

The block transitions may be sharp or tapered.

A tapered transition refers to a piece of the molecular chain in which the monomers of block A form a random distribution with the monomers of block B. The molecular weight desired for the blocks is controlled via the ratio of initiator to monomer.

The disclosed block copolymers with a polymer block derived from monomers of the general formula II mix with crystal or high impact polystyrene to form polymer blends having a raised softening point and good mechanical properties.

In addition, the block copolymers of this invention can be used as such. They are particularly suitable for food contact applications, since their residual monomer content is extremely low, advantageously below 3000 ppm, especially below 2000 ppm, for monomers of the formula I and below 500 ppm, preferably below 200 ppm, for monomers of the formula II.

EXAMPLES

Purification of 1,1-Diphenylethylene (DPE)

Crude DPE (Aldrich or from reaction of phenylmagnesium bromide with acetophenone, acetylation with acetic anhydride and thermal elimination of acetic acid) is distilled through a column having at least 50 theoretical plates (spinning-band column; a Sulzer packed column for larger amounts) to a purity of 99.8%. The usually slightly yellow distillate is filtered through a 20 cm Alox column (Woelm alumina for chromatography, anhydrous), titrated with 1.5N sec-butyllithium to a deep red color and distilled off over a simple still head under reduced pressure (1 mbar). The

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resulting product is completely colorless and can be used directly in the anionic polymerization.

Polymerization

Solutions with living anions were generally handled under ultrapure nitrogen. The solvents were dried over anhydrous alumina.

In the Examples which follow, S represents styrene, DPE represents 1,1-diphenylethylene and the % ages are by weight, unless otherwise stated.

Example 1

Preparation of random S/DPE copolymer with an S-DPE molar ratio of 2:1; simultaneous addition of S, DPE and cyclohexane

A 2 l glass reactor equipped with a jacket for cooling and heating and a horseshoe stirrer was inertized for several hours with a refluxing solution of DPE/sec-butyllithium in cyclohexane. After removal of the cleaning solution, 100 ml of cyclohexane, 100 ml of a mixture of 264.24 ml (270.38 g, 1.5 mol) of DPE and 344.37 ml (312.45 g, 3.0 mol) of styrene and also 9.71 ml of 0.5M sec-butyllithium solution in cyclohexane were introduced as initial charge at 25° C. The mixture at once turned red. The reactor contents were thermostated to 70° C. by means of the heating jacket, the heating greatly deepening the color of the solution. The remaining 508.6 ml of the S-DPE mixture were metered in over 40 min via an injection pump at a constant rate. At the same time 500 ml of cyclohexane were run in over the same period.

7 min after completion of the addition a further 249 ml of cyclohexane were added (polymer concentration 50%). The viscosity increased distinctly during the polymerization. After a further 15 min of postreaction time, the contents were titrated with ethanol to a colorless endpoint, the polymer was precipitated in ethanol by dropwise addition of the polymer solution, filtered off and repeatedly washed with boiling ethanol, and the resulting white powder was dried at 180° C. under reduced pressure (1 mbar) for 2 h.

Yield: 580 g (99.5%); volatiles: 0.3%; styrene content (FTIR): 54.5% (53.6% theor.); DPE content (FTIR): 45.1% (46.4% theor.); level of monomeric DPE (component B) 2180 ppm, level of styrene (component C) 384 ppm; Tg (DSC): 155° C.; range of glass transition stage: 9° C.; molar masses (GPC, polystyrene calibration, g/mol): Mn 105,000, Mw 126,000, M(peak maximum) 119,000.

Example 2

Preparation of a random S/DPE copolymer with an S-DPE molar ratio of 2:1; initial charge of DPE and cyclohexane and addition of S

The reactor prepared as in Example 1 was charged at 25° C. with 749 ml of cyclohexane, 264.24 ml (270.38 g, 1.5 mol) of DPE and 9.71 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. The first 300 ml of styrene were metered in over 5 min, the next 20 ml over 10 min and the remaining 24.37 ml of styrene over 15 min. After a postreaction time of 15 min the batch was worked up as described in Example 1.

Yield: 582 g (99.8%); volatiles: 0.1%; styrene content (FTIR): 54.1% (53.6% theor.); DPE content (FTIR): 45.5% (46.4% theor.); DPE monomer (component B): 350 ppm, styrene monomer (component C): 25 ppm; Tg (DSC): 156° C.; range of glass transition stage: 12° C.; molar masses (GPC, polystyrene calibration, g/mol): Mn 107,000, Mw 128,000, M(peak maximum) 120,000.

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Example 3

Preparation of a random S/DPE copolymer with an S-DPE molar ratio of 1.1:1; initial charge of DPE and addition of S and cyclohexane

The reactor prepared as in Example 1 was charged at 25° C. with 264.24 ml (270.38 g, 1.5 mol) of DPE and 7.37 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. 189.4 ml (171.85 g, 1.65 mol) of styrene were premixed with 810.6 ml of cyclohexane. The mixture was metered in over 180 min by means of an injection pump by reducing the rate of addition according to a gradient method. The amounts added were:

0-30 min	507.94 ml;
30-60 min	253.97 ml;
60-90 min	126.98 ml;
90-120 min	63.49 ml;
120-150 min	31.75 ml;
150-180 min	15.87 ml.

After a postreaction time of 15 min, the batch was worked up as described in Example 1.

Yield: 441 g (99.7%); volatiles: 0.1%; styrene content (FTIR): 39.2% (38.9% theor.); DPE content (FTIR): 60.9% (61.1% theor.); DPE monomer (component B): 560 ppm; styrene monomer (component C): 12 ppm; Tg (DSC): 173° C.; range of glass transition stage: 13° C.; molar masses (GPC, polystyrene calibration, g/mol): Mn 104,000, Mw 124,000, M(peak maximum) 116,000.

Example 4

Preparation of an S/DPE-S diblock copolymer with an S-DPE molar ratio for the S/DPE block of 1.1:1.

The reactor prepared as in Example 1 was charged at 25° C. with 264.24 ml (270.38 g, 1.5 mol) of DPE and 14.74 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. 189.4 ml (171.85 g, 1.65 mol) of styrene were premixed with 810.6 ml of cyclohexane. The mixture was metered in over 90 min by means of an injection pump by reducing the rate of addition in the form of a gradient as described in Example 3.

Following a postreaction time of 15 min, 442.2 g of styrene and 400 ml of cyclohexane were metered in over 15 min and the batch was worked up as described in Example 1 after a further 15 min.

Yield: 884 g (99.9%); volatiles: 0.05%; styrene content (FTIR): 69.4% (69.4% theor.); DPE content (FTIR): 30.5% (30.6% theor.); DPE monomer (component B): 72 ppm; styrene monomer 7 ppm; Tg (DSC, two equally high glass transition stages): 171° C.; width of glass transition stage: 15° C.; 105° C.; width of glass transition stage: 16° C. Molar masses (GPC, polystyrene calibration, g/mol): Mn 115,000, Mw 123,000, M(peak maximum) 119,000.

Example 5

Preparation of an S/DPE-S-S/DPE triblock copolymer with an S-DPE molar ratio for the S/DPE blocks of 1.1:1 and coupling with ethyl formate

The reactor prepared as in Example 1 was charged at 25° C. with 264.24 ml (270.38 g, 1.5 mol) of DPE and 29.48 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. 189.4 ml (171.85 g, 1.65 mol) of styrene were premixed with 810.6 ml of cyclohexane. The mixture was metered in over 60 min by means of an injection pump by reducing the

rate of addition in the form of a gradient as described in Example 3. After a postreaction time of 10 min, 442.2 g of styrene and 400 ml of cyclohexane were metered in over 15 min. After a further 15 min, 546 mg of ethyl formate in 2 ml of cyclohexane were added dropwise to the point of complete decolorization. The polymer was worked up as described in Example 1.

Yield: 884 g (99.9%); volatiles: 0.05%; styrene content (FTIR): 69.4% (69.4% theor.); DPE content (FTIR): 30.5% (30.6% theor.); DPE monomer (component B): 381 ppm; styrene monomer (component C): 5 ppm; Tg (DSC, two equally high glass transition stages): 169° C.; width of glass transition stage: 17° C.; 106° C.; width of glass transition stage: 18° C. Molar masses (GPC, polystyrene calibration, g/mol): main peak M(peak maximum) 121,000, 72% area; secondary peak M(maximum) 60,000, 28% area.

Example 6

Preparation of random S/DPE copolymer with an S-DPE molar ratio of 1.1:1; initial charge of DPE and addition of S and tetrahydrofuran (THF)

The reactor prepared as in Example 1 was charged at 25° C. with 264.24 ml (270.38 g, 1.5 mol) of DPE and 7.37 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. 189.4 ml (171.85 g, 1.65 mol) of styrene were premixed with 810.6 ml of THF. The mixture was metered in over 180 min by means of an injection pump by reducing the rate of addition in the form of a gradient as described in Example 3.

After a postreaction time of 15 min, the batch was worked up as described in Example 1.

Yield: 403 g (91.2%); volatiles: 3.7%; styrene content (FTIR): 42.6% (38.9% theor.); DPE content (FTIR): 57.3% (61.1% theor.); Tg (DSC): 159° C.; range of glass transition stage: 17° C.; molar masses (GPC, polystyrene calibration, g/mol): Mn 87,000, Mw 111,000, M(peak maximum) 108,000.

Example 7

Preparation of random S/1,1-di(3,4-dimethylphenyl)ethylene copolymer having an S-di(3,4-dimethylphenyl)ethylene molar ratio of 1.1:1; initial charge of di(3,4-dimethylphenyl)ethylene and addition of S and cyclohexane

The reactor prepared as in Example 1 was charged at 25° C. with 355.5 g (1.5 mol) of freshly melted 1,1-di(3,4-dimethylphenyl)-ethylene and 8.79 ml of 0.5M sec-butyllithium solution and thermostated to 70° C. 189.4 ml (171.85 g, 1.65 mol) of styrene were premixed with 810.6 ml of cyclohexane. The mixture was metered in over 180 min by means of an injection pump by reducing the rate of addition in the form of a gradient as described in Example 3.

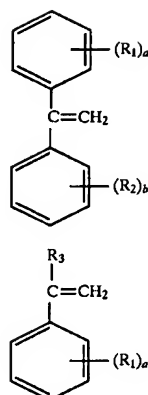
After a postreaction time of 15 min, the batch was worked up as described in Example 1.

Yield: 525 g (99.5%); volatiles: 0.2%; styrene content (FTIR): 32.7% (32.6% theor.); DPE monomer (component B): 65 ppm; styrene monomer (component C): 9 ppm; Tg (DSC): 175° C.; width of glass transition stage: 14° C.; molar masses (GPC, polystyrene calibration, g/mol): Mn 36,000, Mw 90,000, M(peak maximum) 89,000.

We claim:

1. A thermoplastic molding, composition of

A) from 10 to 100% by weight of a copolymer consisting essentially of the monomers of the general formulae I and II



where

R_1 is H or alkyl of 1-22 carbon atoms,

R_2 is H or alkyl of 1-22 carbon atoms,

R_3 is H or alkyl of 1-4 carbon atoms,

a is 0, 1, 2, 3, 4 or 5, and

b is 0, 1, 2, 3, 4 or 5

as obtained by providing the monomers of the formula (I) as initial charge and metering in the monomers of the formula II during the reaction according to a gradient method such that, as the reaction progresses, the amount of monomer (II) added per unit time is essentially reduced according to the amount of monomer (I) still present;

B) from 0 to 3000 ppm, based on the weight of component a, of compounds of the general formula I;

C) from 0 to 500 ppm, based on the weight of component A, of compounds of the general formula II;

D) from 0 to 90% by weight, based on the total weight of the molding compound, of polymers other than A); and E) from 0 to 50% by weight, based on the total weight of the molding compound, of additives and processing aids.

2. Thermoplastic molding composition as claimed in claim 1, comprising from 0 to 1000 ppm of component B), based on the total weight of component A).

3. Thermoplastic molding composition as claimed in claim 1, comprising from 0 to 100 ppm of component B), based on the total weight of component A).

4. Thermoplastic molding composition as claimed in claim 1, comprising a copolymer of 1,1-diphenylethylene and styrene as component A.

5. A process for producing a copolymer (A), as described in claim 1, consisting essentially of the monomers of the general formulae (I) and (II) by anionic polymerization, which comprises providing the monomers of the formula (I) as initial charge and metering in the monomers of the formula (II) during the reaction according to a gradient method such that, as the reaction progresses, the amount of monomer (II) added per unit time is essentially reduced according to the amount of monomer (I) still present.

6. A process as claimed in claim 5, wherein the refractive index of the reaction mixture is continuously determined during the reaction and monomer II is added according to a gradient method as a function of the change in the refractive index.

7. Block copolymers with blocks A and B of the following general structure:



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B—A—B

X [(A—B)_n]_m, X [(B—A)_n]_m, X [(A—B—A)_n]_m, or
 X [(B—A—B)_n]_m

where

A is a block of copolymers of monomers of the general
 formulac I and II,

B is a block of monomers of the general formula II,

X is the radical of an m-functional coupling agent,

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n is an integer from 1 to 5, and

m is an integer from 2 to 20.

8. Thermoplastic molding compounds comprising as
 5 essential components a block copolymer as claimed in claim
 7, 0–3000 ppm of monomers of the general formula I and
 0–500 ppm of monomers of the general formula II.

* * * * *

[54] PREPARATION OF BRANCHED BLOCK COPOLYMERS

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[52] U.S. Cl. 525/314

[58] Field of Search 525/314

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[57] ABSTRACT

A process for the preparation of branched block copolymers of from 60 to 95% by weight of a monovinyl-aromatic monomer and from 40 to 5% by weight of a conjugated diene by polymerizing the monomers in an

inert solvent in the presence of a monolithium-hydrocarbon as the initiator, wherein, in a first process stage (a), from 50 to 80, or where necessary at most 90, % by weight of the total amount of monovinyl-aromatic compound are polymerized to virtually complete conversion in the presence of a relatively small amount of the monolithium-hydrocarbon. This stage is carried out by starting with from 30 to 70% by weight of the vinyl-aromatic monomer and adding from 70 to 30% by weight in the feed, during the polymerization, in such a way that the polymerization temperature, which at the start of the polymerization is from 30° to 40° C., is kept at from 45° to 70° C., with use of reflux cooling. After all the monomer feed has been added, the reaction temperature is lowered to 30°–40° C. by evaporative cooling. In a second process stage (b), an additional amount of initiator is added to the reaction solution, after which from 1 to 30% by weight of the total amount of monovinyl-aromatic monomer can be added, the sum of the amounts of monovinyl-aromatic monomer added in the first and second process stages being at most 90% by weight of the total amount of monovinyl-aromatic monomer. The monovinyl-aromatic monomer added in the second process stage is polymerized to virtually complete conversion, employing the temperature profile described for stage (a). In process stage (c), the remainder of the monovinyl-aromatic monomer and all of the conjugated diene are added, at least predominantly in the form of a mixture, and polymerized so that the reaction temperature does not rise above 90°–110° C. Finally, after virtually complete conversion of the monomers, and preferably without prior cooling, a suitable liquid polyfunctional coupling agent is run in undiluted and the mixture of the linear block copolymers obtained, which still contain active terminal lithium-carbon bonds, is coupled, with stirring, to form branched block copolymers. The products prepared according to the invention are used for injection molding.

1 Claim, No Drawings

PREPARATION OF BRANCHED BLOCK COPOLYMERS

The present invention relates to a process for the preparation of branched block copolymers of from 60 to 95% by weight of a monovinyl-aromatic monomer and from 40 to 5% by weight of a conjugated diene by polymerizing the monomers in an inert solvent in the presence of a monolithium-hydrocarbon as the initiator, with stepwise addition of monomer and initiator and subsequent coupling of the resulting living linear block copolymers with a polyfunctional coupling agent.

The relevant prior art includes (1) U.S. Pat. No. 4,086,298 and (2) U.S. Pat. No. 4,167,545.

(1) and (2) disclose the preparation of branched block copolymers having a polymodal distribution. The products obtained by the known processes have greater transparency and better mechanical properties than pure polystyrene or mixtures of polystyrene with linear block copolymers. In particular, they are superior in respect of impact strength and yield stress to the products known from German Laid-Open Application DOS No. 1,959,922.

It is an object of the present invention to improve the transparency and impact strength of the products known from (1) and (2). Both properties are adversely affected by chain termination reactions during polymerization, which lead to homopolystyrene and to non-coupled two-block copolymers. The chain termination has a particularly adverse effect on the transparency of mixtures of standard polystyrene and products obtained according to (1) or (2).

We have found that this object is achieved by the measures set out in the characterizing clause of claim 1.

By employing the temperature profile described in the characterizing clause of claim 1, the proportion of homopolystyrene can be substantially reduced and the coupling yield increased. The use of undiluted coupling agent moreover further increases the coupling yield and accordingly further improves the impact strength. Accordingly, the products prepared by the process according to the invention show improved processing stability and heat resistance. The processing range is broadened and the upper limit, for preservation of transparency, of the molecular weight of polystyrene which can be used as a component in the mixture is raised. Furthermore, finished articles show no clouding on annealing. The surface quality of extruded sheet can be further improved by admixture of lubricants.

Examples of monovinyl-aromatic monomers suitable for the process according to the invention are styrene, sidechain-alkylated styrenes, e.g. α -methylstyrene, and nuclear-substituted styrenes, e.g. vinyltoluene and ethylvinylbenzene. The monovinyl-aromatic monomers can be employed individually or as a mixture with one another. Preferably, styrene, by itself, is employed.

Examples of conjugated dienes which can be employed, individually or as mixtures with one another, in the process according to the invention for the preparation of the branched block copolymers are butadiene, isoprene and 2,3-dimethylbutadiene. Butadiene and isoprene are particularly preferred, and of these two, in turn, butadiene is preferred.

The branched block copolymers prepared by the process according to the invention should in total contain, as copolymerized units, from 60 to 95% by weight, especially from 70 to 90% by weight, of the monovinyl-

aromatic monomer and from 40 to 5% by weight, preferably from 30 to 10% by weight, of a conjugated diene, in each case based on the total monomers employed. The molecular weight of the branched block copolymer should as a rule be from 100,000 to 1,000,000 and is preferably from 150,000 to 500,000.

The process according to the invention is carried out by successive polymerization of the monomer solution in the presence of a monolithium-hydrocarbon initiator and with stepwise addition of monomer and initiator, the resulting living block copolymers being subsequently coupled by means of a polyfunctional, reactive compound. Accordingly the method is as follows:

In a first process stage (a), a non-elastomeric polymer segment is first produced, in which a substantial proportion of the total amount of the monovinyl-aromatic monomer is polymerized by means of a relatively small amount of the monolithium-hydrocarbon initiator in an inert solvent under the conditions which will be described below.

From 50 to 80, or if necessary up to 90, % by weight of the total amount of monovinyl-aromatic monomer is used. In process stage (a), from 0.1 to 10 millimoles of lithium catalyst/mole of the monovinyl-aromatic monomer employed in the first process stage are used.

The initiator used is a conventional monolithium-hydrocarbon of the general formula RLi , where R is an aliphatic, cycloaliphatic, aromatic or aliphatic-aromatic hydrocarbon radical. Preferably, monolithium-alkyl compounds, where alkyl is of 2 to 6 carbon atoms, are employed, n-butyl-lithium and sec.-butyl-lithium being particularly preferred.

Suitable hydrocarbon solvents are aliphatic, cycloaliphatic or aromatic hydrocarbons which are liquid under the reaction conditions and which preferably are of 4 to 12 carbon atoms. Specific examples are isobutane, n-pentane, isooctane, cyclopentane, cyclohexane, cycloheptane, benzene, toluene and xylene. Mixtures of these solvents can also be employed. Furthermore, it is possible to carry out the polymerization in the presence of small amounts of ethers, such as tetrahydrofuran, in order to influence, in a conventional manner, the polymerization rate, the configuration of the butadiene polymer segments and the transition between the segments of the different monomers. Preferably, however, the reaction is carried out without addition of ether. The concentration of the monomers in the reaction solution is not critical and can be adjusted so that any desired polymerization apparatus can be employed. Usually, the polymerization is carried out in a 10-30% strength solution in the inert solvents.

The polymerization is carried out under the conventional conditions for anionic polymerization with lithium-organic compounds, such as the presence of an inert gas atmosphere, and exclusion of moisture. To establish anhydrous conditions, any moisture present is first titrated with lithium-organic compounds.

It is essential in carrying out process stage (a) to observe a certain temperature profile over the period up to the second addition of initiator. This can be achieved, for example, by starting the polymerization at a certain temperature, in the range of from 30° to 40° C., and removing the heat of reaction generated, using evaporative cooling and at the same time introducing monomer through the feed, the temperature being kept below 80° C. and in particular at from 45° to 70° C. A skilled worker can readily calculate, from the heat of reaction to be expected, the ratio of vinyl-aromatic monomer

respectively to be used in the initial charge and in the feed in process stage (a). If the polymerization is started at 30°–40° C., it is possible, for example, to employ from 30 to 70% by weight of the total vinyl-aromatic monomer to be reacted in process stage (a) as the initial charge, whilst the remainder, namely from 70 to 30% by weight, can be added during the polymerization in process stage (a). It is particularly preferred to regulate the feed of monomer, under given conditions of reflux cooling, to maintain a temperature of from 45° to 70° C.

After completion of the addition of the vinyl-aromatic monomer the polymerization temperature is next lowered, by evaporative cooling, to from 30° to 40° C., before the second addition of initiator is made. This lowering of the temperature is a precondition for carrying out process stage (b) or, if the latter is omitted, carrying out the subsequent process stage (c).

The polymerization in the first process stage (a) is taken to virtually complete conversion of the monovinyl-aromatic monomer employed. This gives a solution of non-elastomeric, living polymer of the monovinyl-aromatic monomer, i.e. polymer segments with active terminal lithium-carbon bonds, which are capable of further addition reaction with monomer.

In the second process stage (b)—if such a stage is carried out—a further amount of fresh initiator is added to the solution obtained in process stage (a). This amount should be as great, or greater, than the original amount of initiator employed in the first process stage (a) of the polymerization. Preferably, the additional amount of initiator added in the second process stage is from 1 to 15, and especially from 1 to 10, times as great as the amount of initiator originally employed.

In this process stage, after addition of the initiator, it is possible to add, if necessary, from 1 to 30% by weight, preferably from 5 to 20% by weight, of the total amount of the monovinyl-aromatic monomer used for the process according to the invention. The sum of the amounts of monovinyl-aromatic monomer employed in the first stage and, where relevant, in the second stage should however be at most 90% by weight of the total amount of the monovinyl-aromatic monomer. If a further amount of monovinyl-aromatic compound is added in the second process stage, a temperature profile is maintained, in the manner described above [cf. process stage (a)], by reflux cooling and by dividing the calculated amount of monomer appropriately between the initial charge and the feed. Accordingly, in process stage (b) the same conditions in respect of heat removal are employed as in process stage (a). At the end of process stage (b), the polymerization temperature is again lowered to a value within the range of from 30° to 40° C. by employing reflux cooling. (If, however, after addition of initiator in process stage (b), no additional amount of vinyl-aromatic monomer is added, the process stage described under (c) below can follow immediately). In process stage (b), as in the first process stage (a), the polymerization is taken to virtually complete conversion of the monovinyl-aromatic monomer added. This has the effect that in addition to the chains resulting from addition to polymer segments formed in the first process stage, new chains of living polymers are also formed (polymodal synthesis).

In a further processing stage (c), polymer segments containing diene are polymerized onto the active chain ends. During the polymerization of the total amount of the conjugated diene plus any residual monovinyl-aromatic monomer still present, the temperature should

not exceed 110° C. The heat of polymerization is generated within a brief period, so that suitable measures must be taken to prevent this limit of 110° C. from being exceeded. Preferably, the temperature at the end of the last process stage (before the coupling is carried out) is from 90° to 110° C. One measure of ensuring this is to lower the temperature sufficiently, by employing reflux cooling in stages (b) and/or (a), before starting stage (c). Another possible measure is to add part of the diene, especially butadiene, in the feed, and then to add the remaining monomers, i.e. diene and vinyl-aromatic monomer, as a mixture, all at once, to the reaction batch. To achieve the desired structure, it is necessary that the predominant proportion of the monomers to be polymerized onto the chains in process stage (c) is added direct, as a mixture of diene and vinyl-aromatic monomer, to the polymerization batch. In process stage (c), the total amount of conjugated diene, i.e. from 5 to 40% by weight of the total monomers employed, is used. The amount of vinyl-aromatic monomer used in this stage depends somewhat on how much of the monomer has been used in process stage (b), if such a stage has been operated.

After completion of polymerization of the monomers or monomer mixture in the last process stage (c), the reaction solution contains a mixture of living linear block copolymers having reactive lithium-styryl carbon bonds.

The mixture of these living, linear block copolymers is then reacted, in a further process step, in the presence of a polyfunctional reactive compound as a coupling agent. For the process according to the invention, the coupling agent must be at least trifunctional. Examples include polyepoxides, such as epoxidized linseed oil, polyisocyanates, for example benzene-1,2,4-trisocyanate, cyclic anhydrides, such as maleic anhydride, polyketones and polyhalides. Dicarboxylic acid esters, for example diethyl adipate or the like, can also be used as coupling agents. The silicon polyhalides are a further group of suitable coupling agents. Further, polyfunctional coupling agents based on divinylbenzene can be employed. Epoxidized linseed oil is particularly preferred as the coupling agent.

The coupling of the living linear block copolymer with the polyfunctional coupling agent is carried out within a narrow temperature range, namely at from 90° to 110° C. It is necessary not to exceed the stated upper limit, since otherwise the yield diminishes. Liquid coupling agents which are not less than trifunctional and can be dosed as liquids under the coupling conditions are particularly preferred. We have found, surprisingly, that adding the coupling agent in undiluted form, with stirring, leads to an increase in yield. Accordingly, the process according to the invention is preferably carried with addition of the liquid coupling agent *tel quel*. Following the coupling reaction, but advantageously before isolating the star-branched polymer from the reaction solution, the polymer (mixture) can, if desired, be selectively or completely hydrogenated, in a manner known to a skilled worker.

The branched block copolymer is isolated from the reaction solution in a conventional manner, for example by precipitating and filtering off.

The products prepared by the process according to the invention can be directly processed by conventional thermoplastic processing methods, i.e. by, for example, extrusion, injection molding, calendering, blow-molding, compression-molding or sintering. The production

of injection moldings and of packaging materials is particularly preferred. To produce these moldings and packaging materials, the products obtained by the process according to the invention are preferably mixed with other thermoplastics, especially with standard polystyrene, in the proportions familiar to a skilled worker. We have found that the products prepared by the process according to the invention can be compounded with polystyrenes of higher molecular weight than has been disclosed to be the case for prior art products (cf. (1) or (2)). Surprisingly, even finished articles made from such mixtures show no clouding on annealing. If desired, conventional additives can be introduced into the products, obtained according to the invention, before or during processing. The same is true of the preparation of blends with other thermoplastics.

Suitable additives include stabilizers, fillers, colored pigments, external lubricants, plasticizers, antistatic agents and blowing agents, which are employed in the conventional amounts known to a skilled worker. To improve the surface quality of extruded films, external lubricants used are, for example, octadecyl alcohol, butyl stearate, microcrystalline wax or Acrawax.

The parameters described in the Examples and Comparative Experiments were measured as follows:

1. The intrinsic viscosity, measured in 0.5% strength by weight solution in toluene at 25° C., is shown as a measure of the molecular weight, more precisely of the weight-average molecular weight, of the block copolymers.

2. The damaging energy in [N.m] was determined according to DIN 53,453 on an injection molding.

3. The impact strength, a_n , in kJ/m², was determined according to DIN 53,413.

The invention is illustrated below by an Example and Comparative Experiments. All parts and percentages quoted therein are by weight, unless stated otherwise.

EXAMPLE AND COMPARATIVE EXPERIMENTS

The experiments described below were carried out in a polymerization kettle of 1.5 m³ capacity, and using a total amount of 200 kg of monomers. Cyclohexane was used as the solvent in every case. The solids concentration after completion of polymerization was 25%. The coupling agent used was epoxidized linseed oil in every case. When working up the reaction product, 1.5 parts of trinonyl phosphite, as a stabilizer, and 0.5 part of tert.-butyl-phenol were added.

COMPARATIVE EXPERIMENT A

Example 1 of prior art (1) was carried out in a pressure reactor of 6 liters capacity.

Repeating this Example, in a polymerization kettle of 1.5 m³ capacity, without special measures for removing heat, gave a temperature of 90° C. after the first polymerization stage, and 120° C. at the end of the second stage. After cooling the mixture to 90° C. by jacket cooling, the coupling agent was added, as a 10% strength solution in toluene, in a single shot. The intrinsic viscosity of the reaction product was found to be 75.6 cm³/g. The mechanical properties are shown in the Table, together with values obtained from the other experiments, as a function of the injection molding temperature. The column headed "Homopolystyrene" in the Table furthermore shows the content of homopolystyrene, in % by weight, formed by chain termination reactions. This proportion is based on the total product

and was determined by selective extraction with a mixture of methyl ethyl ketone and acetone.

COMPARATIVE EXPERIMENT B

Example 1 of German Published Application DAS No. 1,959,922 was repeated. According to the statements of the applicant, Example 1 was probably carried out in an autoclave of about 15 liters capacity. On repeating this Example in the polymerization kettle of 1.5 m³ capacity, the final temperature was found to be 96° C. at the end of the first process stage, 85° C. at the end of the second stage and 125° C. at the end of the third stage. Before adding the diluted coupling agent, the batch was cooled to 85° by jacket cooling. The intrinsic viscosity of the polymer obtained was 78.2 cm³/g.

EXAMPLE 1

This Example describes the process according to the invention without addition of vinyl-aromatic monomer in process stage (b).

In a polymerization kettle of 1.5 m³ capacity, equipped with a reflux condenser, 600 kg of cyclohexane and 60 kg of styrene were titrated with n-butyllithium at 35° C., under an inert gas atmosphere and with exclusion of moisture, until polymerization commenced. 2.0 moles of sec.-butyl-lithium, as a solution in cyclohexane, were then added. As a result of the polymerization starting, the internal temperature rose to 59° C. 40 kg of styrene were then run in at 60° C. in the course of 15 minutes, with operation of reduced pressure evaporative cooling. After completion of the polymerization, the mixture was further cooled to about 40° C. by reduced pressure evaporative cooling. After addition of a further 2.26 moles of sec.-butyl-lithium and a mixture of 50 kg of styrene and 50 kg of butadiene, the internal temperature rose to 98° C. in the course of 20 minutes. Immediately after the maximum temperature had been reached, 560 g of epoxidized linseed oil, in the liquid state, were introduced in the course of 10 minutes, with stirring, and the reaction solution was then cooled to room temperature, mixed with stabilizer and worked up. The intrinsic viscosity of the product obtained was found to be 78.5 cm³/g.

COMPARATIVE EXPERIMENT C

Experiment C was carried out similarly to Example 1, but the coupling agent was only added (as a 10% strength solution in toluene) after cooling the polymerization solution to 70° C. The intrinsic viscosity of the product obtained was 73.1 cm³/g.

The Table shows that the products obtained by the process according to the invention exhibit a better pattern of properties.

TABLE

Com- para- tive Experi- ment	Exam- ple	Homopoly- Styrene [%]	Injection molding tempera- ture	Damaging energy N/m	Impact strength KJ/M ²
A	—	14.7	200	13.5	26.4
			220	13.5	18.9
			240	12.6	15.2
			260	11.5	11.5
			280	11.2	8.7
—	1	5.9	200	27.8	no fracture
			220	24.5	24.3
			240	32.4	18.9
			260	32.4	14.6
			280	28.9	13.3

TABLE-continued.

Com- para- tive Experi- ment	Exam- ple	Homopoly- Styrene [%]	Injection molding tempera- ture	Damaging energy N/m	Impact strength KJ/M ²
B	—	16.8	200	13.0	24.1
			220	13.5	18.1
			240	14.3	13.4
			260	14.6	10.1
			280	12.9	9.3
C	—	6.5	200	11.8	19.7
			220	11.6	16.4
			240	11.7	12.0
			260	11.6	11.8
			280	5.9	7.6

We claim:

1. A process for the preparation of branched block copolymers of from 60 to 95% by weight of a monovinyl-aromatic monomer and from 40 to 5% by weight of a conjugated diene of 4 to 8 carbon atoms by polymerizing the monomers in an inert solvent in the presence of a monolithium-hydrocarbon as the initiator, wherein, in a first process stage (a), from 50 to 80, or where necessary at most 90, % by weight of the total amount of monovinyl-aromatic compound are polymerized to virtually complete conversion in the presence of a relatively small amount of the monolithium-hydrocarbon, and thereafter, in a second process stage (b), an additional amount of initiator, which may be equal to or greater than the originally employed amount of initiator, is added to the reaction solution, after which a further 1-30% by weight of the total amount of monovinyl-aromatic monomer can be added, the sum of the amounts of monovinyl-aromatic monomer added in

the first and second process stages being at most 90% by weight of the total amount of monovinyl-aromatic monomer, and any such monovinyl-aromatic monomer added in the second process stage is polymerized to virtually complete conversion, after which, in a further process stage (c), the remainder of the monovinyl-aromatic monomer and all of the conjugated diene are added, at least predominantly in the form of a mixture, and are polymerized, and finally, after virtually complete conversion of the monomers, the mixture of the resulting linear block copolymers, having active terminal lithium-carbon bonds, is subjected to coupling by addition of a polyfunctional coupling agent, with stirring, to form branched block copolymers, in which process 30-70% by weight of the total amount of vinyl-aromatic monomer to be reacted in process stage (a) is initially taken and 70-30% by weight is added, in the feed, during the polymerization in such a way that the polymerization temperature, which at the start of the polymerization is from 30° to 40° C., is kept at from 45° to 70° C., with use of reflux cooling, during stage (a), after completion of the monomer feed the reaction temperature is lowered to 30°-40° C. by evaporative cooling before fresh initiator is added in order to carry out stage (b) or (c); if stage (b) is carried out, the same temperature profile as for stage (a) is employed, and furthermore the polymerization of the remaining vinyl-aromatic monomer and the conjugated diene in stage (c) is carried out in such a way that the reaction temperature does not rise above 90°-110° C., and finally, after completion of the polymerization, and preferably without prior cooling, a suitable liquid coupling agent is run undiluted into the reaction mixture.

* * * * *

Morphology and Dynamic Viscoelastic Behavior of Blends of Styrene-Butadiene Block Copolymers

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Different block length distributions in styrene-butadiene block copolymers of the linear SBS or (SB)₂ "star" type and their mixtures can cause wide changes in domain morphology at constant overall monomer composition (75 wt % styrene). Block polymers of substantially uniform block length had the expected spherical, polystyrene-continuous morphology. Broadening the styrene block length distribution by blending polymers of different block lengths led to appearance of cylindrical and lamellar structures and, ultimately, to complex polybutadiene-continuous morphologies. Polymers and blends were characterized by electron microscopy and by their viscoelastic behavior. Correlations were established between morphology on one hand and anisotropy in the storage modulus and the height and position of the polybutadiene $\tan \delta$ maximum on the other.

When a block copolymer is blended with the homopolymer of one of the monomers of which it is composed, the homopolymer will enter the block polymer domain structure only when its molecular weight does not greatly exceed that of the block sequences of like composition (1,2). When it does so, the homopolymer forms its own, usually much larger, domains which may absorb some of the like-block sequences in their surface regions.

In the present study we examine the situation where both constituents of the blend are block copolymers of the same two monomers, but where the block lengths may vary widely between constituents. As a

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constraint on the enormous number of such blends possible, the total composition of the blend is held fixed. The monomers chosen are styrene and butadiene at an overall blend composition of 75% styrene (by weight).

Experimental

Block polymers were prepared by organolithium-initiated polymerization in cyclohexane solution by using the sequential monomer addition technique (3). Polymers were both of the linear-SBS and "radial"-branched (SB)₂ type. Blends were prepared in cyclohexane solution, either before or after coupling the initially linear SBLi precursor. Coupling agents investigated were ethyl acetate (for linear coupling), epoxidized soybean oil (ESO), and SiCl₄.

Block molecular weights were calculated from monomer charges and initiator levels and corrected for "scavenger level," i.e., the amount of RLi destroyed by system impurities. These nominal block lengths were, in general, in good agreement with gel-permeation chromatographic molecular weights.

Block length polydispersity indices for blends were calculated on the assumption that the block polymers, as prepared, were composed of monodisperse blocks. This is, of course, an approximation justified only by the narrowness of the molecular weight distribution in polymerizations of the present type. The block heterogeneity indices given here should, therefore, be regarded as relative measures of breadth of distribution.

Polymers and blends were worked up by evaporating the cyclohexane solvent and massing the polymer on a 140°C roll mill. Films were then prepared by compression molding (5 min at 200°C) or, in one set of experiments, by extrusion through a slit die. Dynamic viscoelastic meas-

Table I. Blend Compositions

Compo- sition	Compo- nent	Wt Fraction	Precoupling		Styrene (%)	$(\bar{M}_w/\bar{M}_n)_s$
			$\bar{M}_n/1000$	Block Length $\bar{M}_s/1000$		
A	—	1.00	19	56	75	1
	1	0.64	30	120	80	
B	2	0.36	7.6	13.4	63.8	2.4
	Blend	1.00	—	—	74.2	
C	1	0.64	13	137	91.3	
	2	0.36	11	10	47.6	3
	Blend	1.00	—	—	75.7	
D	1	0.64	6	144	96.3	
	2	0.36	13.5	7.5	35.9	3.5
	Blend	1.00	—	—	74.5	
E	1	0.64	—	150	100	
	2	0.36	14.9	6.1	29.1	3.7
	Blend	1.00	—	—	74.5	

Results

Table I describes five compositions, each of 75% styrene content, prepared by coupling diblock SBLi molecules of varying block length with a polyfunctional epoxide. The data are arranged in order of increasing

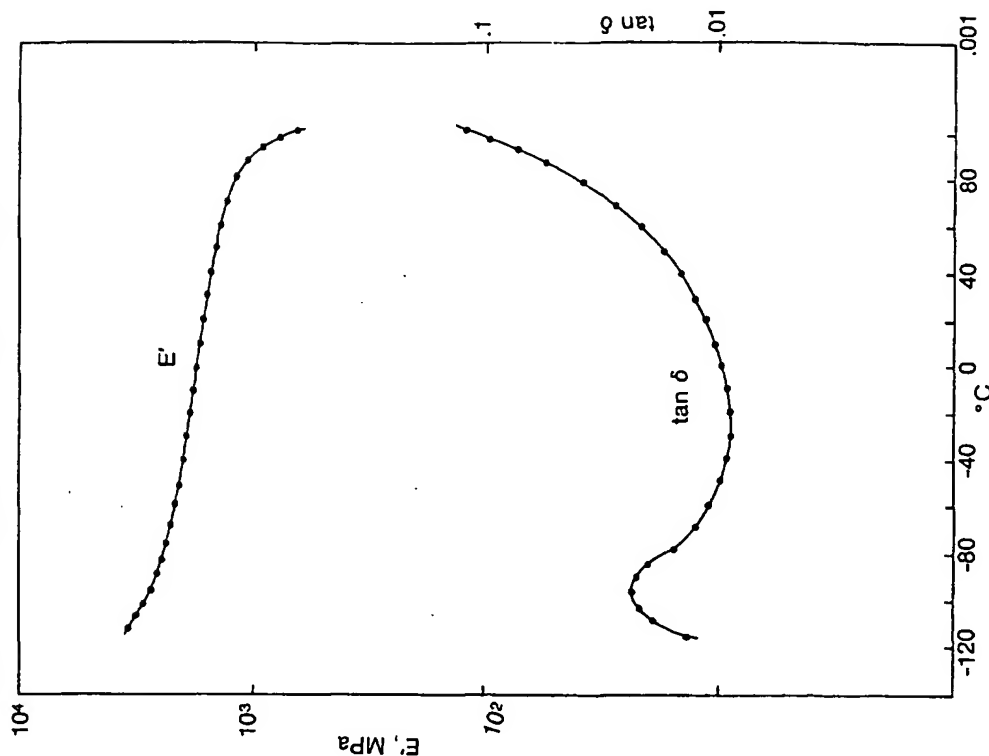


Figure 1. Storage modulus and loss tangent (35 Hz) for block polymer with uniform polystyrene blocks (composition A). Compression molded.

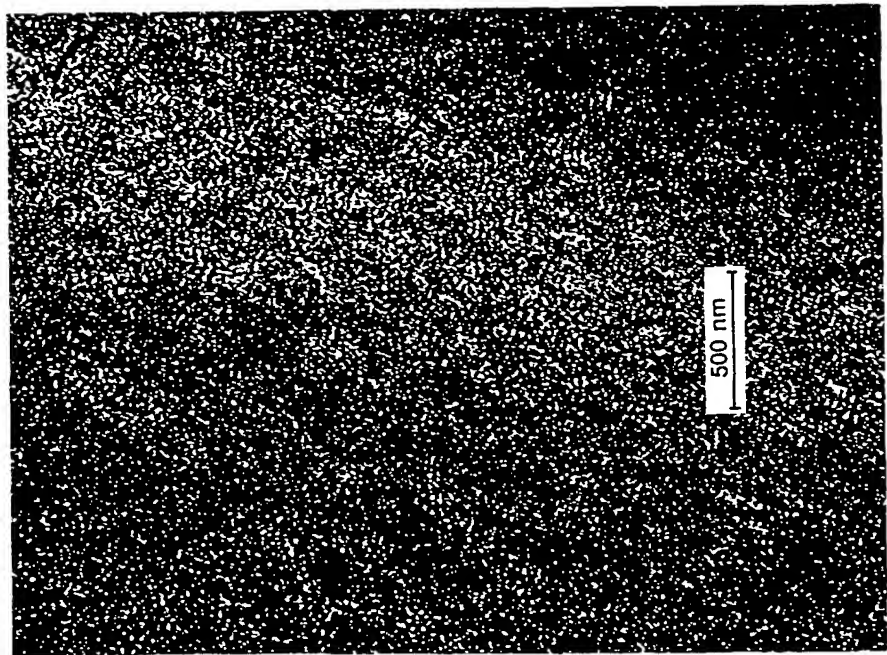


Figure 2. Electron micrograph of composition A

ing polydispersity of (nominal) polystyrene (PS) block lengths. While the polybutadiene (PB) blocks also vary in length, their polydispersity is considerably less.

Figure 1 shows storage modulus and loss tangent vs. temperature plots for composition A, which is not a blend. As shown by Figure 2, the morphology is spheres of PB in a continuum of PS. The loss tangent clearly shows the PB glass transition at -90°C and the ascending branch of the PS maximum near 100°C . The results are exactly as expected from the spherical morphology, except that the temperature of the PB $\tan \delta$ maximum lies several degrees lower than that of polybutadiene of the appropriate microstructure (ca. 50% trans, 40% cis, and 10% vinyl) for which $T(\tan \delta_{\max}) \cong -80^{\circ}\text{C}$.

Figure 3 shows the same kind of data for blend C, in which PB block lengths are similar, but the PB blocks differ greatly in length; Figure 4 shows an electron micrograph of this composition. The morphology of this blend is clearly lamellar, with considerable orientation in one direction. (The uneven spacings of light and dark bands result from lamellae sectioned at various angles.) The direction of orientation is that of mold flow. The dynamic data are entirely consistent with this

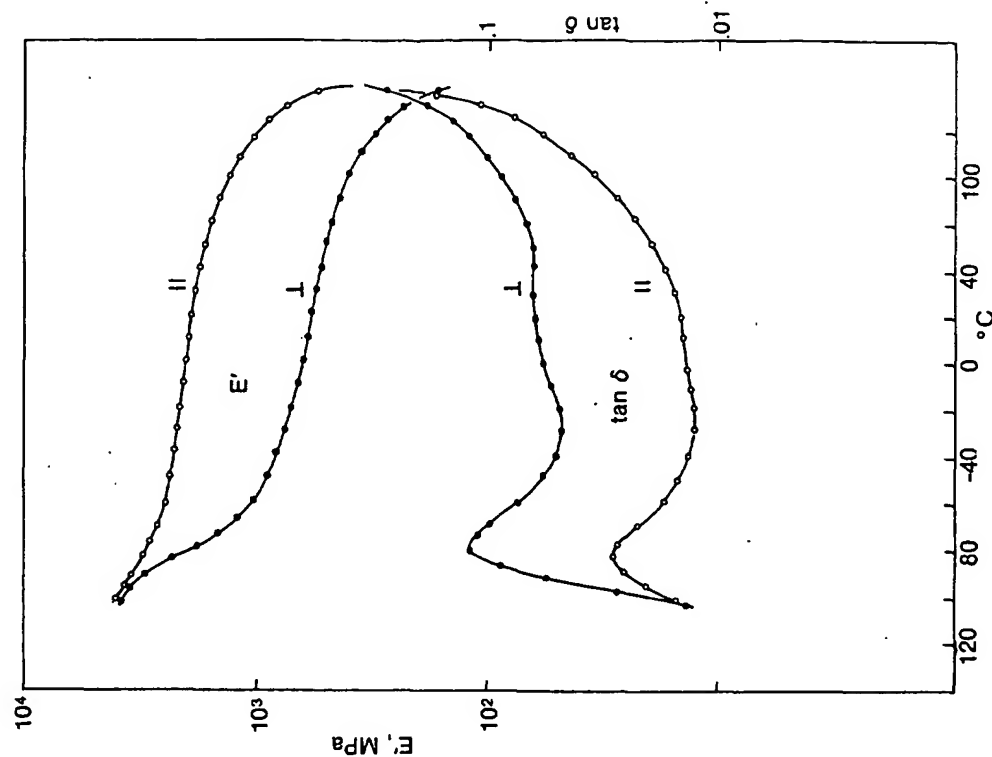


Figure 3. Storage modulus and loss tangent (35 Hz) for composition C with bimodal polystyrene block length distribution (composition C). Compression molded: (||) parallel to direction of mold flow; (\perp) normal to direction of mold flow.



Figure 4. Electron micrograph of composition C

morphology. In the direction of mold flow, E' and $\tan \delta$ are not too greatly different from Figure 1 but normal to the flow direction, the resin is much softer (smaller E'), and the PB $\tan \delta$ peak is strongly accentuated.

The above results are for compression-molded samples. A closer investigation of these resins in extruded film is summarized in Figures 5 and 6. Note the relative isotropy in mechanical properties characteristic of the spherical morphology for the single polymer and the strong anisotropy for the blend. Note also that for the lamellar blend $T(\tan \delta_{\max})$ is consistently -80° to -81°C , the normal value for polybutadiene independent of orientation. The reason for the depression of $T(\tan \delta_{\max})$ in the single polymer is evidently the constraint the polybutadiene

domains find themselves under as the result of differences in thermal contraction of the phases as they cool from T_g (polystyrene). The smaller coefficient of expansion of glassy polystyrene causes the cavities accommodating the polybutadiene inclusions to shrink less than the free contraction of polybutadiene, placing the latter phase in a state of hydrostatic tension and lowering T_g . In the lamellar morphology there is no such constraint; the polybutadiene lamellae merely thin out and the

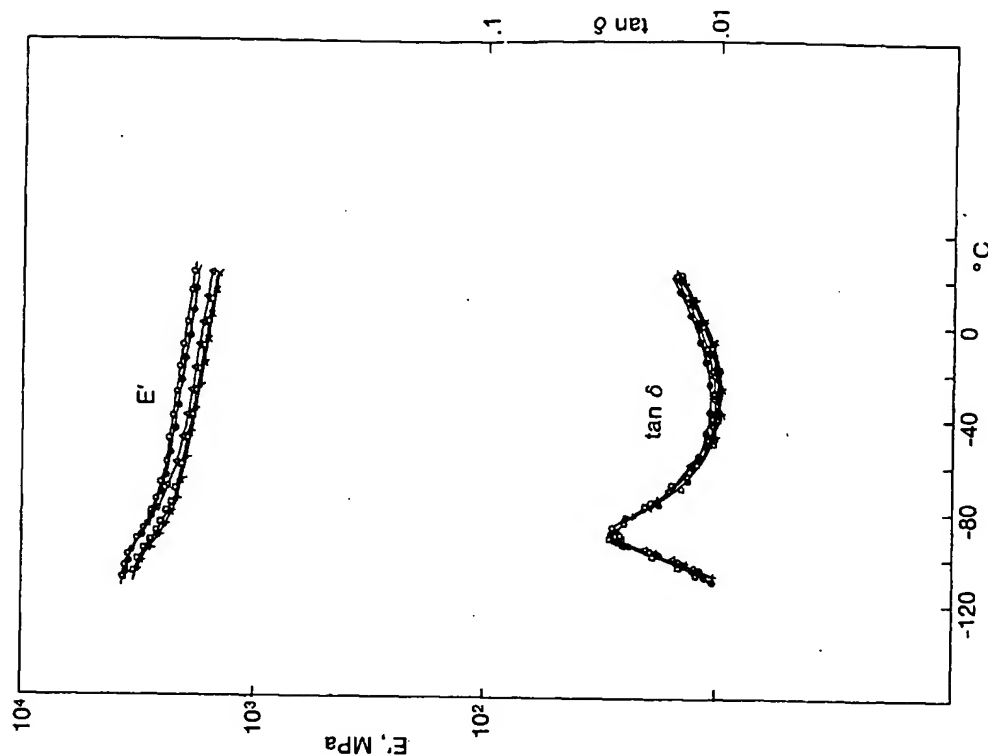


Figure 5. Effect of orientation on E' and $\tan \delta$ in extruded film (35 Hz) of composition A. Direction of measurement with respect to extrusion direction: (O) 0° , (●) 22.5° , (Δ) 45° , (□) 67.5° , (X) 90° .

is a summary of the principal morphology-related features of the dynamic viscoelastic data, clearly confirm the different morphologies. The rod-like PB domains of Figure 7 cause only modest anisotropy since PS remains continuous in both directions of orientation. $T(\tan \delta)$ is again depressed, as cylindrical PB domains cannot contract freely under the constraint of the glassy continuum.

Electron micrographs of compositions D and E are shown in Figures 9 and 10. It is evident that in E polybutadiene is the continuous phase (with some rubber in the polystyrene domains) while D represents a transition from lamellar to polybutadiene-continuous morphology. Again the dynamic mechanical data (Table II) are consistent with these obser-

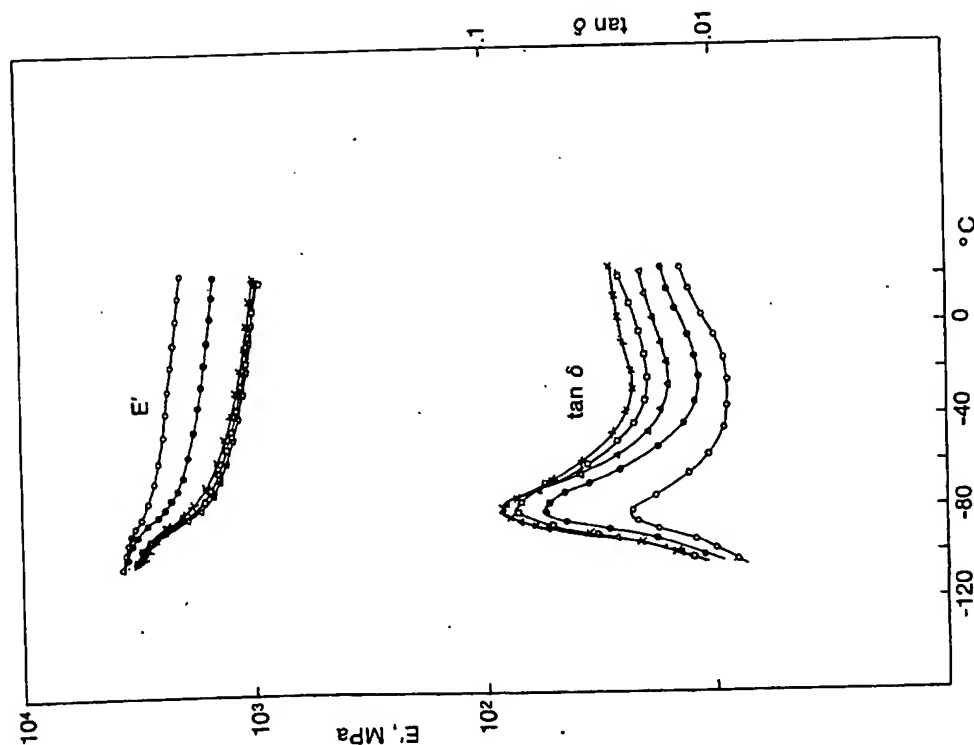


Figure 6. Effect of orientation on E' and $\tan \delta$ in extruded film (35 Hz) of composition C. Notation as in Figure 5.

normal T_g is observed. Comparison of Figures 3 and 6 indicates the degree of orientation to be greater in the compression-molded sample.

Returning now to composition B, in which the PS block distribution is less severe than in C, we note that evidently both rod-like and lamellar morphologies are about equally probable. The morphologies shown in Figures 7 and 8 were obtained on presumably identically prepared samples; they appear to be the result of small adventitious variations in molding technique and/or thermal history. The data of Table II, which

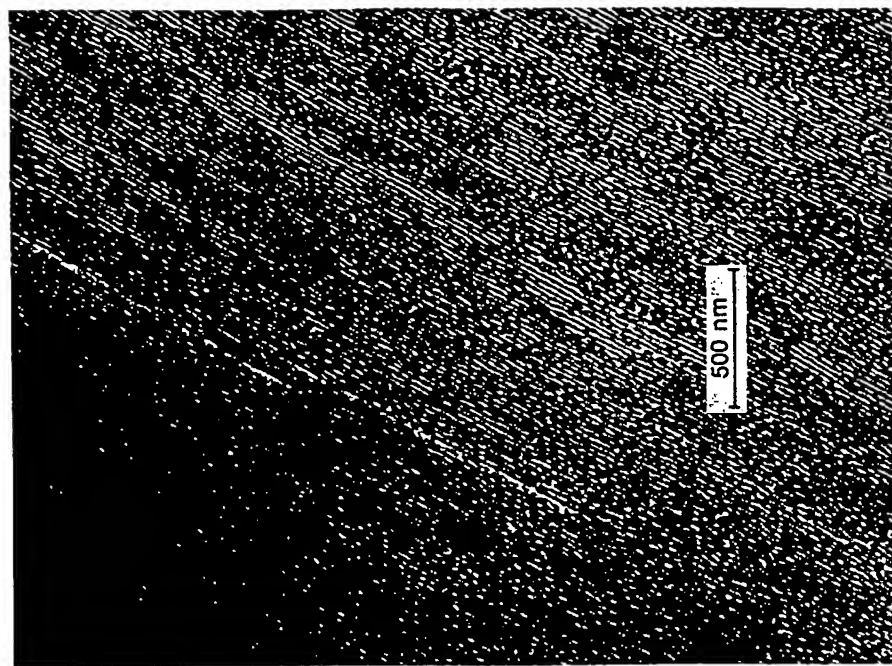


Figure 7. Composition B in rod-like form

Table II. Morphology and

Resin	$(\bar{M}_w/\bar{M}_n)_s$	Continuous Phase	Discrete Phase
A	1.0	PS	PB (spheres)
B ^a	2.4	PS	PB (rods)
			alternating lamellae
C	3		alternating lamellae
D	3.5	PB ^a	PS (complex
E	3.7	PB	PS (ellipsoids)

^a Compression-molded samples.

^b E'_{20} = storage modulus at 20°C.

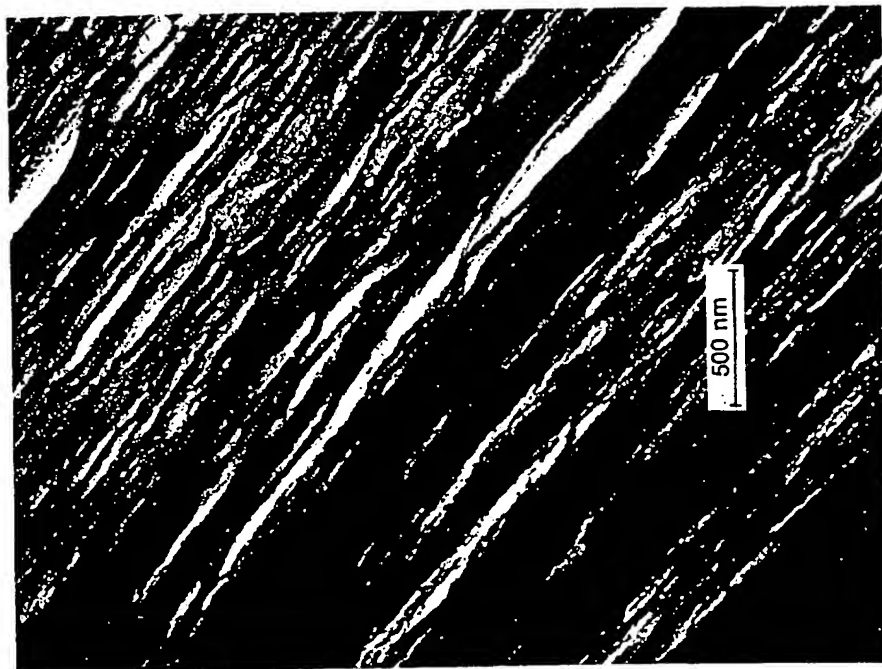


Figure 8. Composition B in lamellar form

Dynamic Viscoelastic Properties^a

Parallel to Flow ^b			Normal to Flow ^b		
$\tan \delta_{max}$	$T(\tan \delta_{max})$ (°C)	E'_{20} (MPa)	$\tan \delta_{max}$	$T(\tan \delta_{max})$ (°C)	E'_{20} (MPa)
0.021	-94	1760	0.026	-94	1680
0.024	-90	1550	0.044	-90	1300
0.061	-84	1260	0.137	-83	520
0.030	-80	1850	0.120	-80	530
0.181	-76	330	0.244	-76	170
0.296	-79	140	0.300	-78	130

^a This composition has been observed in two distinct morphologies; see text.

^b Predominantly.

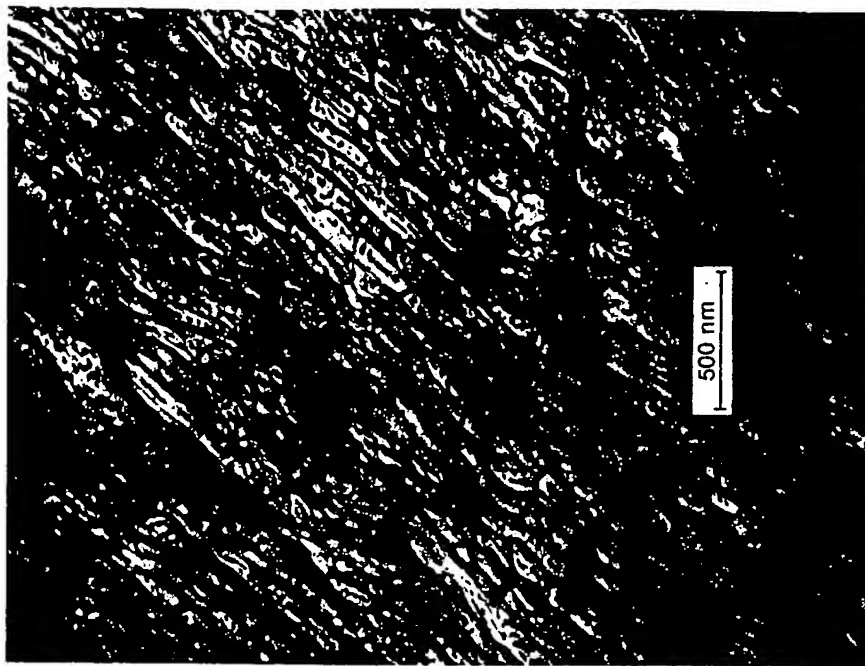


Figure 9. Morphology of composition D

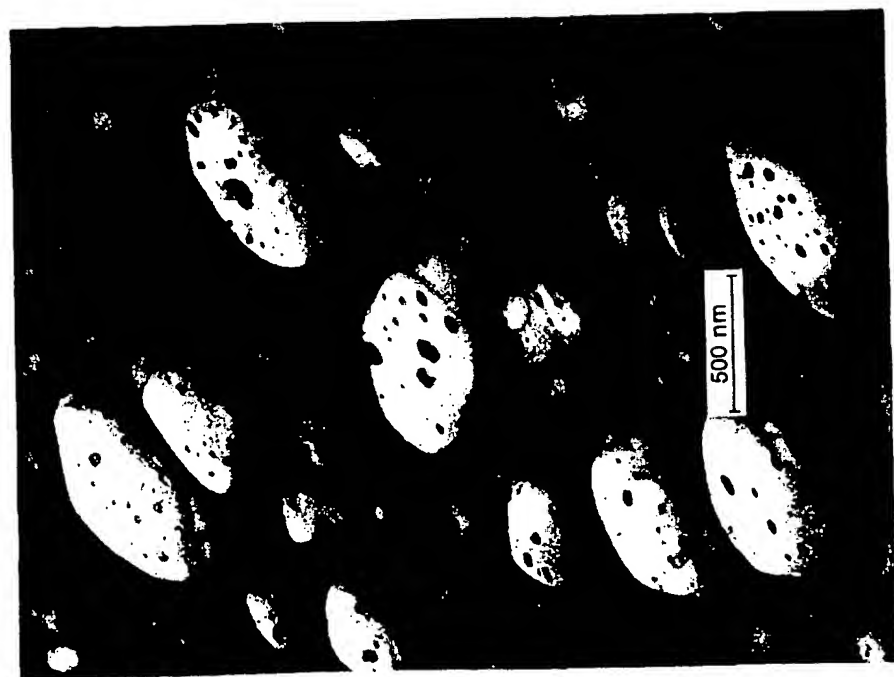


Figure 10. Morphology of composition E

vations, showing much smaller storage moduli and large $\tan \delta$ maxima near -80°C for the PB domains. Mechanical anisotropy is absent in E.

The above results show clearly that, in the system at hand, the broader the distribution of PS block length, the greater the tendency of the minor PB phase to become continuous. It is also obvious that the dynamic mechanical data tell a great deal about the morphology. The height of the PB loss maximum increases as the rubber becomes increasingly load bearing while at the same time E' (between the transitions) decreases. Mechanical anisotropy resulting from orientation is most pronounced for the lamellar structure. Finally, the position of the polybutadiene $\tan \delta$ peak is depressed for those morphologies in which polystyrene is the continuous phase.

Some seventy blends were examined by dynamic viscoelastic measurements only. They differed in molecular weight of the constituents, linearity of the constituent block polymer molecules, (SBS vs. [SB] $_{\text{L}}$), type and stoichiometry of coupling, order of coupling (before and after blending), composition of the fractions, and blend ratio—always, however, subject to the constraint of 75% styrene content. Although differences in viscoelastic behavior were observed, the most decisive variable by far was block-length heterogeneity. Figure 11 shows a plot of the height of the $\tan \delta$ maximum vs. $(\bar{M}_w/\bar{M}_n)_s$. One can easily spot the ranges of block heterogeneity in which different morphologies are to be expected. This pattern is confirmed by Figure 12 in which the height of $\tan \delta$ is plotted against its position. There are several reasons, aside from experimental error, for the variability in properties at equal $(\bar{M}_w/\bar{M}_n)_s$. One is that \bar{M}_w/\bar{M}_n is only one of many possible, nonequivalent ways of expressing block length heterogeneity and is not necessarily the most relevant one to the present situation. Also, as in Table I, in the expanded study the PB blocks do vary in size, even if much less than the PS blocks. Lack of morphological uniqueness, as in blend B, complicates the picture in the overlap region near $\bar{M}_w/\bar{M}_n = 2.5$. Finally, there is a tendency for abnormally high $T(\tan \delta_{\text{max}})$ in the compositions with the broadest PS block distribution. Attainment of such distributions requires use of substantial amounts of polymer with PS blocks of less than 10,000

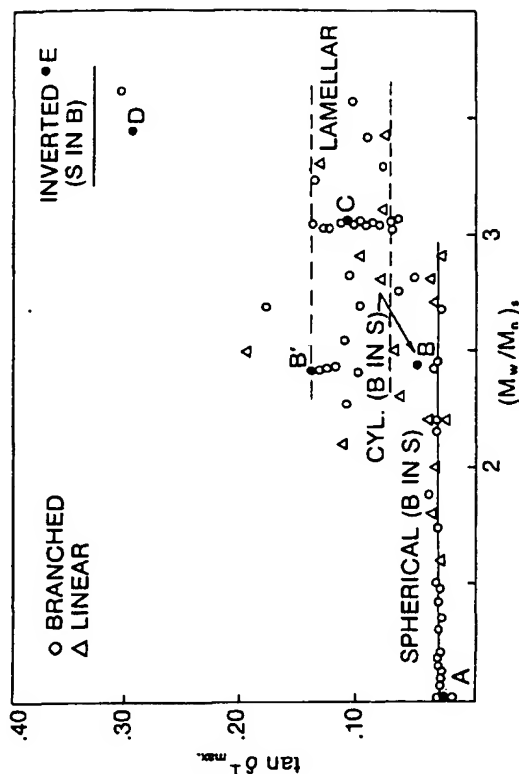


Figure 11. Maximum low temperature loss tangent (35 Hz) measured normal to mold flow vs. styrene block length heterogeneity. Circles—branched polymers, triangles—linear polymers, solid symbols—electron micrographs displayed.

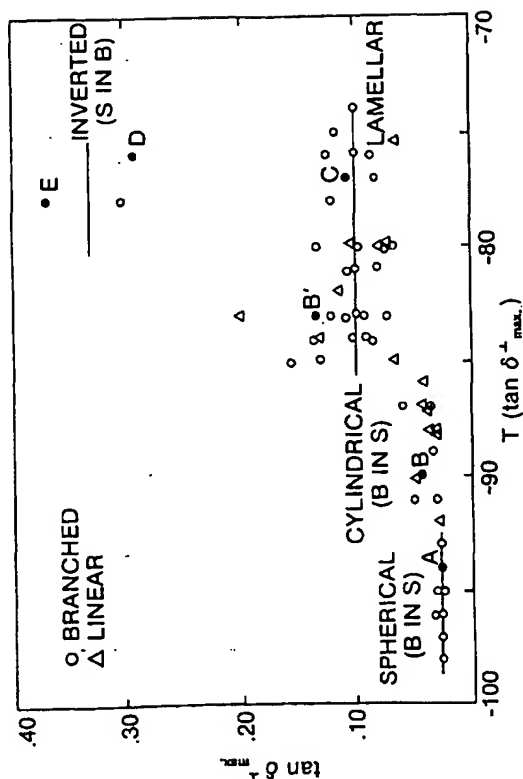


Figure 12. Height and position of low temperature loss maximum. Notation as in Figure 11.

molecular weight (5000 was the shortest block used in this work). In this range of block molecular weights, interphase effects begin to have an effect on the position of the PB loss maximum (5).

Extreme differences in PB block length curiously appear to extend the range in PS block heterogeneity in which polystyrene-continuous morphologies are possible. For example, Figure 13 shows a straight blend of linear SBS polymers in which both kinds of blocks vary tenfold in length (composition F):

Wt Fraction	S/B/S	Styrene (%)	$(\bar{M}_w/\bar{M}_n)_s$
Component 1	0.60	150000/100000/150000	75 (1)
Component 2	0.40	15000/10000/15000	75 (1)
Blend	1.00	—	75 2.9

In spite of $(\bar{M}_w/\bar{M}_n)_s = 2.9$, the morphology appears to be basically spherical, albeit with considerable connectivity of polybutadiene domains. Moreover, for this blend $\tan \delta_{\max} = 0.028$, $T(\tan \delta_{\max}) = -88^\circ\text{C}$, with virtually no anisotropy in storage modulus, consistent with spherical or short rod-shaped polybutadiene domains.

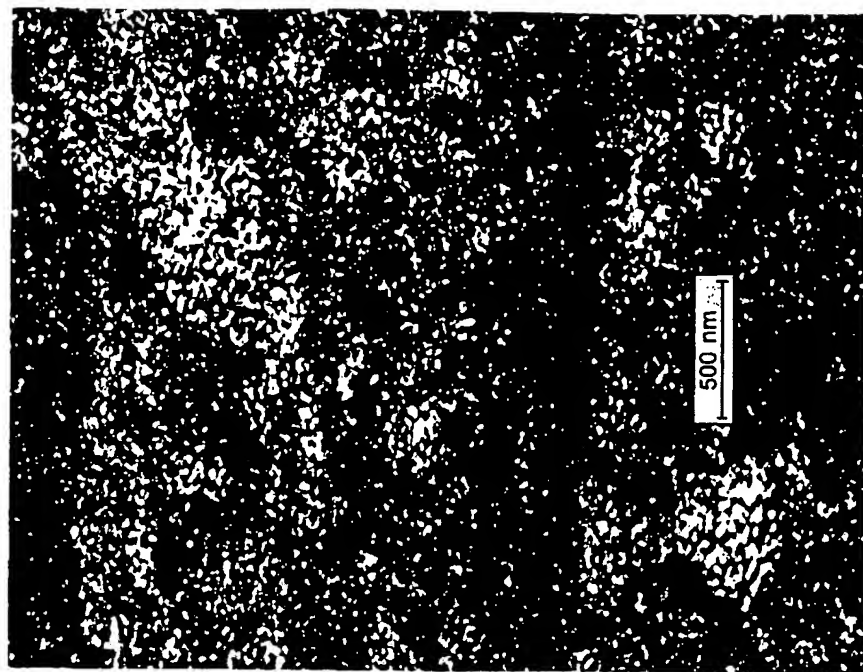


Figure 13. Morphology of composition F

Discussion

The observation that broad, bimodal styrene, block length distributions tend to favor continuity of the polybutadiene phase is not confined to 75% styrene content. Thus, a limited study at 50% styrene showed that polybutadiene-continuous compositions could be prepared by broad blending in place of the normal alternating lamellar structures characteristic of this composition.

Since simple blending of the finished block polymers and coupling blends of SBLi di-block polymers did not produce markedly different results, it seems clear that the block length distribution per se is more

important in governing morphology than the disposition of these blocks over individual molecules.

Extensive use is made in this work of the effects of orientation on mechanical properties in block polymers with cylindrical and lamellar structures. These effects are, in general, known from earlier studies (6,7); they add convincing evidence to the morphological assignments made.

It should be clear that the conclusions of this work are limited to block polymers isolated from the polymerization solvent (cyclohexane) by evaporation and subsequently processed by conventional thermal mixing and shaping techniques. Obviously, other morphologies could be realized in many instances by casting films from solvents of varying quality for the two block sequences.

Conclusions

Different block length distributions in SBS and (SB)₂ block polymers and their mixtures can cause wide changes in domain morphology at constant overall monomer composition, which lead to characteristically different linear viscoelastic properties.

Acknowledgment

The authors are indebted to J. O. Gardner for the electron micrographs displayed in this report.

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Poly(Arylene Ether Sulfone)-Poly(Aryl Carbonate) Block Copolymers

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The influence of block molecular weight and slightly varying chemical compositions on microphase separation in poly(arylene ether sulfone)-poly(aryl carbonate) block copolymers was examined. Compositional variety was achieved by replacing the isopropylidene unit in the bisphenol-A derived aryl sulfone blocks by either a thiol or a sulfonyl group. Synthetic methods and characterization techniques were used that allowed careful control of average block size in these [AB]_n copolymer systems, all of which were overall 50% by weight of each type segment. Although physical blends of the homopolymers are incompatible, DSC and mechanical measurements indicated that either one- or two-phase films could be molded from the block copolymers. Kinetic effects regulating the formation of two phases from the melt were observed.

Multiphase polymeric materials very often are based on either graft copolymers or block copolymers. It is interesting to note that graft copolymers have been largely associated with impact thermoplastic technology whereas block copolymers have to date found most of their practical applications in the form of thermoplastic elastomers (1-8). We have been interested in studying ductile glassy-glassy and glassy-crystalline block copolymers as models for homogeneous and multiphase engineering materials. Very little quantitative experimental information is available concerning the important parameters governing the development of the microphases in such systems. Qualitatively, block molecular weight and segment interaction parameters most likely are important. Secondly, almost nothing is known with respect to the effect of microphase development on mechanical properties such as ductility, impact strength, environmental stress cracking, and physical aging.

KINETICS OF ALKYL LITHIUM INITIATED POLYMERIZATIONS

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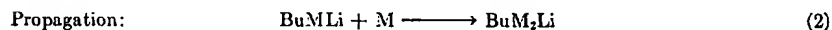
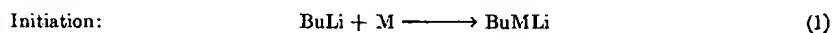
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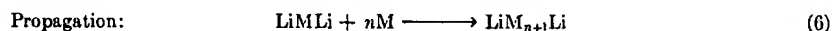
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I. INTRODUCTION

The polymerization of vinyl monomers with alkali metals was reported as early as 1910-1914 by Mathews and Strange¹, Harris², and Schlenk³. Ziegler⁴ in 1929 first described the polymerization of butadiene in the presence of *n*-butyllithium (*n*-Buli) and in 1936 in a review article Ziegler⁵ proposed mechanisms which describe the polymerizations by metallic lithium and butyllithium. The mechanisms consisted of initiation and propagation steps, and it was recognized that termination and transfer reactions may not contribute significantly. For butyllithium-initiated polymerization, the following mechanism was proposed:



In metal-initiated polymerization, it was suggested that the initial reaction produced an intermediate having two active propagation centers which could add monomers at both ends.



In subsequent years anionic polymerization received little attention in contrast

to the remarkable advance in the understanding of polymerization during the same period. Lack of interest in studies of anionic polymerization was at least partly associated with such studies. Handling of these initiators is difficult and, to obtain reproducible results, all traces of impurities such as water, oxygen, and alcohol solvent. The limited use of organometal-initiated polymerization discouraged studies of this kind.

However, in 1956, Firestone⁶ announced that polyisoprene to natural rubber had been synthesized by using Hsieh and Tobolsky⁷ reported that high *cis*-polyisoprene alkyl lithium in heptane or benzene. The stereospecificity stimulated and regenerated interest in alkyl lithium. During the last decade, intensive research in this field has taken place in industrial laboratories as well as in academic institutions. A large number of articles published and patents issued in this field are a cause of its versatility and many unique features, and are now being produced commercially by alkyl lithium.

The kinetics of polymerizations of conjugated dienes with alkyl lithium initiators have been extensively studied because they are homogeneous, "living" (*i.e.*, without termination, reaction), and the initiation and propagation steps are simple. On the other hand, these studies are complicated by the low concentration of the alkyl lithium compound in a solvent, usually in the 10^{-4} to 10^{-2} molar range, which makes it difficult to ascertain the exact concentration of the products from the impurities often affect the kinetic results obtained was often made difficult by insufficient concentration of organolithium compounds, particularly in very dilute solutions.

Considerable contradictions and confusions were reported. Good progress has been made in the last few years. This review brings the subject up to date, to discuss the areas investigated, to present an unbiased view seeking to clarify the observations reported in the literature and, hopefully, to provide a basis for further research.

II. STRUCTURE OF ORGANOLITHIUM

It is fundamental to a discussion of the kinetics of polymerizations that we consider the present state of knowledge of the initiator compounds, especially in those solvents where they are presently available. Although one may estimate that the true nature of the carbon-lithium bond. Such factors as the solvent, or the concentration range and the reactivity of the lithium species. For this reason, the information now available regarding each of these factors and binding in lithium organics.

Organolithium compounds may be classified according to the nature of the organic group.

Group A—Those compounds with organic groups which are able to stabilize an incipient carbanion formed by deprotonation.

OF ALKYL LITHIUM INITIATED
POLYMERIZATIONS

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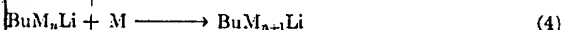
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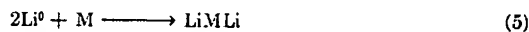
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I. INTRODUCTION

vinyl monomers with alkali metals was reported as early as 1899 by Strange¹, Harris², and Schlenk³. Ziegler⁴ in 1929 first reported the polymerization of butadiene in the presence of *n*-butyllithium. In his review article Ziegler⁵ proposed mechanisms which describe the polymerization of ethylene with metallic lithium and butyllithium. The mechanisms proposed for the propagation steps, and it was recognized that termination steps do not contribute significantly. For butyllithium-initiated polymerization, a termination mechanism was proposed:



From these reactions, it was suggested that the initial reaction produced active propagation centers which could add monomers



Since ionic polymerization received little attention in contrast to anionic polymerization, it was suggested that the initial reaction produced active propagation centers which could add monomers

to the remarkable advance in the understanding of free radical mechanisms of vinyl polymerization during the same period. Lack of interest in mechanistic and kinetic studies of anionic polymerization was at least partly due to experimental difficulties associated with such studies. Handling of these very reactive organometallic initiators is difficult and, to obtain reproducible results, one must eliminate almost all traces of impurities such as water, oxygen, acetylene, etc., in the monomer and solvent. The limited use of organometal-initiated polymerization in technology also discouraged studies of this kind.

However, in 1956, Firestone⁶ announced that *cis*-polyisoprene almost identical to natural rubber had been synthesized by using dispersions of metallic lithium. Hsieh and Tobolsky⁷ reported that high *cis*-polyisoprene could also be prepared with alkyllithium in heptane or benzene. The stereospecificity of isoprene polymerization stimulated and regenerated interest in alkyllithium-initiated polymerizations. During the last decade, intensive research in this area has been done both in industrial laboratories as well as in academic institutions, as witnessed by the large number of articles published and patents issued in recent years. Furthermore, because of its versatility and many unique features, several products were developed and are now being produced commercially by alkyllithium initiation.

The kinetics of polymerizations of conjugated diene and styrene monomers with alkyllithium initiators have been extensively studied. These systems are attractive because they are homogeneous, "living" (i.e., without termination and transfer reaction), and the initiation and propagation steps can be separately studied. On the other hand, these studies are complicated by a number of difficulties. The concentration of the alkyllithium compound in a typical polymerization system is extremely low, usually in the 10^{-4} to 10^{-2} molar range. Trace impurities in the system make it difficult to ascertain the exact concentration of the initiator, and reaction products from the impurities often affect the kinetics. The interpretation of the results obtained was often made difficult by insufficient knowledge of the properties of organolithium compounds, particularly in very dilute solution.

Considerable contradictions and confusions were created on this subject although good progress has been made in the last few years. It is our purpose in this review to bring the subject up to date, to discuss the areas of general agreement among the investigators, to present an unbiased view seeking to reconcile some of the diverse observations reported in the literature and, hopefully, to stimulate further research.

II. STRUCTURE OF ORGANOLITHIUM COMPOUNDS

It is fundamental to a discussion of the kinetics of alkyllithium-initiated polymerizations that we consider the present state of knowledge concerning the nature of the initiator compounds, especially in those solvents in which reliable kinetic data are presently available. Although one may estimate that the carbon-lithium bond should be approximately 43% ionic based on electro-negativity considerations⁸, it is apparent that this statement is an oversimplification and may bear little relation to the true nature of the carbon-lithium bond. Such factors as a change in the organic moiety, the solvent, or the concentration range may drastically affect the bonding and the reactivity of the lithium species. For this reason, we shall examine some of the information now available regarding each of these factors as they determine the structure and binding in lithium organics.

Organolithium compounds may be classified into three rather broad categories, according to the nature of the organic group.

Group A—Those compounds with organic groups which would not be expected to stabilize an incipient carbanion formed by dissociation of the carbon-lithium

bond. In this group, we include the simple alkyllithiums such as methyl lithium, the isomeric butyllithiums, *etc.*, all of which apparently are covalent compounds. With the exception of methyl lithium, these compounds are soluble to some extent in hydrocarbon solvents as well as ethers and have rather low vapor pressures in the pure state (butyllithium is a liquid at room temperature with a vapor pressure of ca. 10^{-2} mm Hg at 80°C).

Group B—Those compounds with sp^2 hybridization at the carbon-lithium bond such as aryllithiums and vinyl lithiums. These substances are generally insoluble in hydrocarbon solvents, and for that reason have often been considered as ionic. However, present information indicates that they may be regarded as essentially covalent compounds, although they are more polar than compounds of Group A. The low volatility of this group (as well as that of methyl lithium) is presumably due to intermolecular association between molecular units in the crystalline state.

Group C—Those compounds with organic groups capable of providing significant resonance stabilization of the corresponding carbanion. This group includes benzyl lithiums, allyl lithiums, *etc.* Such compounds are usually infusible solids, soluble only in basic solvents. The exceptions are polystyryl- and polydienyl- compounds resulting from the polymerization of styrene and dienes. The present consensus is that such compounds are essentially ionic compounds, although the degree of "intimacy" of the ion pairs may vary from one solvent to another (*vide infra*).

The structure and bonding of Group A lithium organics is fairly well understood, at least in the pure state and in aliphatic hydrocarbon solvents, as a result of a flourish of research activity during the past decade and one-half. It is clear from these works that alkyllithiums form rather stable aggregates in which carbon-lithium bond order is maximized by the utilization of all valence orbitals of lithium⁹. Although exhaustive data on the subject are not available, present information indicates that only even-numbered degrees of association are allowed¹⁰ and, moreover, that the tetrameric and hexameric forms are preferred in most cases. The geometry of the tetramer, but not the hexamer, has been deduced from X-ray crystallographic data for ethyllithium¹¹ and methyl lithium¹², and is shown schematically in Figure 1. The lithium atoms form a tetrahedron (distorted in ethyllithium) to each face of which is bonded an alkyl group. The nature of the so-called electron deficient bonding in such aggregates has been the subject of several approximate treatments^{10,12,13}. More recently, two LCAO-MO treatments of the $(\text{CH}_3\text{Li})_4$ structure have appeared^{14,15} which provide theoretical confirmation of the stability

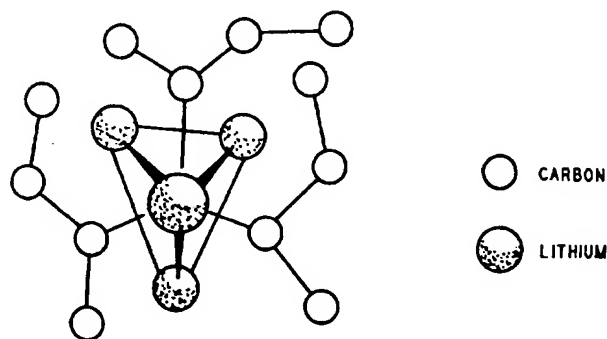


Fig. 1.—View of a model of the *sec*-butyllithium tetramer from above one apex of the lithium tetrahedron. Alkyl group on bottom face of tetrahedron not shown.

of the tetramer in comparison to the dimer and give us some insight into the nature of the driving force. It is clear from these works that carbon-lithium bond order is maximized by the interaction of each carbon atom with lithium atoms. Moreover, it is also significant that carbon in a tetramer structure is substantially less reactive than in the monomeric (or dimeric) form. Thus, the net atomic charge on carbon in methyl lithium monomer are -0.44 and $+0.37$ and for the tetramer -0.34 and $+0.09$ ¹³. The driving force is presumably a driving force in favor of aggregation to decrease the nucleophilicity of the alkyl groups, not including possible steric effects, would be tetramer < dimer < monomer. That is, we would expect the tetramer to be more reactive, an expectation not supported by the available evidence. Figure 1 also shows the repulsions to be experienced by branched alkyl groups. Molecular models suggest that branching of a second atom will cause severe steric hindrance. Thus, *sec*-butyllithium dissociates more than *n*-butyllithium, and the tetramer of *sec*-butyllithium would be expected to be generally found to be quite unreactive compared to the monomer.

Lithium compounds with organic groups which have a negative charge at the carbon atom (Group C compounds) require aggregation for this purpose. Unfortunately, these are insoluble in hydrocarbon solvents, and molecular models suggest only a few cases. Benzyllithium has been reported to form higher aggregates¹⁰, lending credence to the idea that stabilization of the charge leads to lower degrees of association. Molecular weights of polymeric alkyllithiums seem to be low, though in one case, polyisoprenyllithium, there is a high degree of association. As we shall discuss later, Morton¹⁶ reported the compound to be dimeric, while scattering measurements in hexane and aromatic solvents by Bywater¹⁸, however, report a degree of aggregation of about 4, and the basis for the discrepancy is not clear. In cyclohexane¹⁹ and benzene²⁰, polybutadienyllithium shows viscosity measurements¹⁶; however, there is considerable controversy.

There is also still considerable controversy as to the species of Group A lithium alkyls, at least in aliphatic solvents. Some workers have postulated that the monomer is the species at RLi concentrations below $10^{-3} M$ ¹⁷. However, others indicate that alkyllithiums of Group A which are in those solvents without prior dissociation to the monomer. Evidence pertaining to this subject has been obtained from observed ^7Li and alkyl group exchange for trimethyl lithium in cyclopentane.²² The rate of approach to equilibrium is quite low compared to aromatic and aliphatic systems (at 28°C), and the authors consider the principal species to be dimers rather than monomers. Brown²¹ has argued against the use of monomers in mechanistic con-

clude the simple alkyllithiums such as methylolithium, etc., all of which apparently are covalent compounds. Alkyllithium, these compounds are soluble to some extent in ethers and have rather low vapor pressures in the liquid at room temperature with a vapor pressure of

compounds with sp^2 hybridization at the carbon-lithium bond in alkyllithiums. These substances are generally insoluble in ether for that reason have often been considered as ionic. Evidence indicates that they may be regarded as essentially ionic although they are more polar than compounds of Group A. Group A (as well as that of methylolithium) is presumably a transition between molecular units in the crystalline state. Compounds with organic groups capable of providing significant resonance stabilization of the corresponding carbanion. This group includes benzyl- and allyl- compounds. These compounds are usually infusible solids, soluble only in aromatic solvents. They are polystyryl- and polydienyl- compounds. These compounds are usually infusible solids, soluble only in aromatic solvents. The present consensus is that these compounds are essentially ionic compounds, although the degree of ionicity may vary from one solvent to another (*vide infra*).

The chemistry of Group A lithium organics is fairly well understood, at least in aliphatic hydrocarbon solvents, as a result of a flurry of activity during the past decade and one-half. It is clear from the evidence that these compounds form rather stable aggregates in which carbon is coordinated by the utilization of all valence orbitals of lithium⁹. In the subject are not available, present information indicates that the degrees of association are allowed¹⁰ and, more often, hexameric forms are preferred in most cases. The hexamer, but not the hexamer, has been deduced from X-ray diffraction studies of methylolithium¹¹ and methylolithium¹², and is shown schematically in Figure 1. The nature of the so-called electron aggregates has been the subject of several approximate calculations, two LCAO-MO treatments of the $(CH_3Li)_4$ which provide theoretical confirmation of the stability

of the tetramer in comparison to the dimer and monomer, and, more importantly, give us some insight into the nature of the driving forces involved in its formation. It is clear from these works that carbon-lithium bonding is maximized in the tetramer by the interaction of each carbon atom approximately equally with three lithium atoms. Moreover, it is also significant that the residual charge on the carbon in a tetramer structure is substantially less than would be expected for the monomeric (or dimeric) form. Thus, the net atomic charges for carbon and lithium in methylolithium monomer are -0.44 and $+0.37$, for the dimer -0.41 and $+0.20$, and for the tetramer -0.34 and $+0.09$ ¹³. The decrease in net charge at the carbon atom presumably is a driving force in favor of aggregation, and would be expected to decrease the nucleophilicity of the alkyl groups. Thus, the reactivity of aggregates, not including possible steric effects, would be expected to increase in the order tetramer < dimer < monomer. That is, we would expect alkyllithiums which are more dissociated to be more reactive, an expectation which is generally in accord with the available evidence. Figure 1 also shows in crude fashion the possible steric repulsions to be experienced by branched alkyl groups in an alkyllithium tetramer. Molecular models suggest that branching of secondary-alkyllithiums at the β -carbon atom will cause severe steric hindrance. Thus, *sec*-butyllithium would be expected to dissociate more than *n*-butyllithium, and the high reactivity of the former may reflect this tendency. Methylolithium would be expected to be very stable, and is generally found to be quite unreactive compared to *n*-butyllithium.

Lithium compounds with organic groups which are capable of delocalizing the negative charge at the carbon atom (Group C compounds) would presumably not require aggregation for this purpose. Unfortunately, such compounds are generally insoluble in hydrocarbon solvents, and molecular weights have been measured in only a few cases. Benzyllithium has been reported to exist as dimers (rather than higher aggregates) in benzene¹⁰, lending credence to the proposition that resonance stabilization of the charge leads to lower degrees of association. The measured molecular weights of polymeric alkyllithium seem to corroborate this view, as well, although in one case, polyisoprenyllithium, there is some disagreement concerning the degree of association. As we shall discuss in more detail in a later section, Morton¹⁶ reported the compound to be dimeric on the basis of viscosity and light-scattering measurements in hexane and aromatic solvents. Sinn¹⁷, and Worsfold and Bywater¹⁸, however, report a degree of aggregation of four based on similar measurements, and the basis for the discrepancy is not apparent. In the case of polystyryllithium, the various workers seem to agree that the species is dimeric in both cyclohexane¹⁹ and benzene²⁰. Polybutadienyllithium is reported to be dimeric by viscosity measurements¹⁶; however, there is considerable controversy over this number (*vide infra*).

There is also still considerable controversy over the existence of monomeric species of Group A lithium alkyls, at least in aliphatic hydrocarbon solvents. Some workers have postulated that the monomer is the kinetically active species, especially at RLi concentrations below $10^{-3} M$ ¹⁷. However, the bulk of evidence seems to indicate that alkyllithiums of Group A which are soluble in aliphatic solvents react in those solvents without prior dissociation to the monomeric form²¹. Further evidence pertaining to this subject has been obtained by Brown and coworkers who observed 7Li and alkyl group exchange for trimethylsilylmethylolithium and *t*-butyllithium in cyclopentane.²² The rate of approach to exchange equilibrium in this system is quite low compared to aromatic and basic solvents (half-life of ca. 6 hr at $28^\circ C$), and the authors consider the principle exchange mechanism to be one involving dimers rather than monomers. Brown²³ has summarized the arguments against the use of monomers in mechanistic consideration.

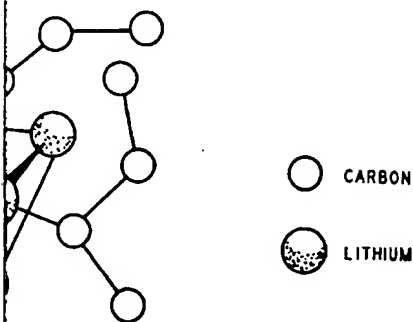


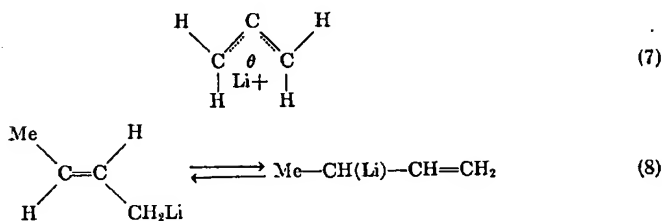
Figure 1. The *sec*-butyllithium tetramer from above one apex of alkyl group on bottom face of tetrahedron not shown.

The picture in aromatic solvents is somewhat less well resolved. Studies by Brown and coworkers have shown that exchange processes are remarkably faster in benzene and toluene^{10,22}. Moreover, there are two lithium compounds, trimethylsilylmethylithium and isopropylithium^{20,24}, whose average degrees of aggregation have been found to be lower in benzene than in cyclohexane. The former has \bar{i} values of 4.0 ± 0.03 and 6.0 ± 0.18 at all concentrations investigated in benzene and cyclohexane, respectively. Isopropylithium reportedly exists as tetramers in both solvents, but with higher aggregates present in cyclohexane solutions above $0.02M$. While the nature of solute-solvent interactions, which are responsible for this effect, have not been elucidated as yet, we may speculate that some type of π -interaction occurs between the aromatic compound and the electron-deficient aggregate. The interaction is accompanied by a shift in the absorption maximum for alkylolithiums from $209 m\mu$ in isooctane²⁵ to $280 m\mu$ in benzene²⁶. Moreover, as mentioned above, one observes greatly increased exchange rates in aromatic solvents²², and corresponding higher rates of chemical reaction. The effect is often remarkable, leading to rate enhancements of 10^3 to 10^4 in benzene or toluene as opposed to cyclohexane²¹.

The structure of organolithium compounds in basic solvents, while not completely elucidated, nevertheless is fairly well understood. It is clear that organolithiums undergo chemical and exchange reactions in basic solvents much more rapidly than in hydrocarbon media¹⁰. This is probably due to increased dissociation of aggregates, and also to an increased polarization of the carbon-lithium bond due to solvent interaction with the lithium atom. The increased dissociation is evidenced by the change of *n*-butyllithium from hexameric form in benzene to tetrameric form in diethyl ether²⁷. Benzyllithium, which is presumably representative of Group C compounds, is monomeric in ether, while phenyllithium in Group B is dimeric²⁷. As mentioned above, polystyryllithium is dimeric in benzene and cyclohexane^{19,20} and monomeric in THF²⁸.

The precise geometry of aggregates in basic solvents, and also the degree of specific solvation of the cation, is still largely a matter of conjecture. Recent nmr results indicate that carbon-lithium bond order is still significant, as evidenced by the presence of ^7Li - ^{13}C spin coupling in methylithium tetramers in ether^{29,30}. However, the lack of ^6Li - ^7Li coupling³¹ suggests that the tetramer structure which is present in the solid state may be perturbed by the basic solvent. A cubic tetramer structure without metal-metal bonding has been discussed^{15,30}.

Recent nmr evidence regarding the nature of allyllithiums in THF has been interpreted largely in terms of delocalized ionic structures³²⁻³⁴. On the other hand, the nmr spectrum of crotyllithium in ether has been interpreted in terms of rapidly equilibrating covalent forms³⁵, with the primary form in preponderance.



Significant information regarding the effect of basic solvents on the structure of Group C organolithiums has come from the group at Syracuse University^{36,37}. Although too lengthy to describe in detail here, the data indicate that such compounds

exist as intimate or solvent separated ion pairs, with as dimeric (or higher) aggregates. The spectral character has been determined, and the fraction of solvent-separated ion pairs has been found to be a sensitive function of the solvating power of the solvent for the metal and organic ions. Solvent-separated ion pairs, although at least one exception found—namely, the metalation of fluorene by *n*-butyllithium in ether mixed solvent²⁹.

The addition of stoichiometric quantities of basic solvents to solutions of alkylolithiums of Group A has been studied rather inconclusively. However, it is clear from the results that the addition of ethers and amines drastically changes the aggregation of the alkylolithium until the ratio of oxygen or nitrogen to lithium is one-half^{38,39}. The conclusion drawn by Eastman and coworkers⁴⁰ that *n*-butyllithium aggregates are formed by the addition of ether is apparently correct. Apparently, each tetramer unit of *n*-butyllithium in one form, although others may be present. Owing to the rapid change in the chemical and physical properties of the accelerating effect of lithium alkoxides on the rate of polymerization, alkylolithiums have been studied by several groups. In general, the effect of such basic salts is to increase the rate of polymerization. The reason is not entirely clear; one may speculate that mixed aggregates of the type $\text{Li}_4\text{R}_3\text{C}$ are formed, providing a higher concentration of reactive species. Early work by Brown and coworkers^{44,45} showed that lithium ethoxide (or triethylamine) to ethyllithium increases the rate of polymerization of the hexameric species. However, it now appears that in one instance the break-up of the *sec*-butyllithium *sec*-butoxide has been observed⁴⁶. We shall discuss more detail in a later section.

In summary, we may characterize organolithiums as polar covalent compounds which prefer to aggregate by lithium bonding, but which may partially dissociate into monomers, or when the organic moiety can convey charge on the carbon atom in monomer units. The stereochemistry of their reactions to be highly dependent on the medium, the substrate, the organic moiety on the monomer, and the concentration range employed. In the subsequent section, we shall discuss the role that each of these factors plays in determining the rate of polymerization of lithium alkyls, and the effect of carbon double bonds.

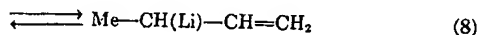
III. RATE OF POLYMERIZATION

Rate of polymerization (R) represents an overall measure of the disappearance of monomer in the polymerization process. In the case of styrene, the polymerization and propagation reactions are occurring simultaneously. The rate of polymerization of styrene in benzene with *n*-butyllithium (or conversion) against time is sigmoidal in shape, as shown by all the investigators (Figure 2). He assumed that each initiator molecule initiates one polymer chain, that there is no te

solvents is somewhat less well resolved. Studies by Brown²⁰ have shown that exchange processes are remarkably faster in ether, and, moreover, there are two lithium compounds, trimethyl-lithium^{20,24}, whose average degrees of aggregation are lower in benzene than in cyclohexane. The former has $\bar{n} = 6.0 \pm 0.18$ at all concentrations investigated in benzene, respectively. Isopropyl-lithium reportedly exists as a monomer with higher aggregates present in cyclohexane. The nature of solute-solvent interactions, which are not yet elucidated as yet, we may speculate that the interaction between the aromatic compound and the electron-accepting lithium is accompanied by a shift in the absorption from 209 m μ in isooctane²⁵ to 280 m μ in benzene²⁶. Furthermore, one observes greatly increased exchange rates in ether, leading to higher rates of chemical reaction. The effect is rate enhancements of 10^3 to 10^4 in benzene or toluene.

Organolithium compounds in basic solvents, while not completely understood, is fairly well understood. It is clear that organo-lithium exchange reactions in basic solvents much more readily than in ether.¹⁰ This is probably due to increased dissociation and increased polarization of the carbon-lithium bond due to the lithium atom. The increased dissociation is evidenced by the change from hexameric form in benzene to tetrameric form in ether, which is presumably representative of Group C compounds, while phenyllithium in Group B is dimeric²⁷. n-Butyllithium is dimeric in benzene and cyclohexane^{19,20}.

Aggregates in basic solvents, and also the degree of dissociation, is still largely a matter of conjecture. Recent nmr studies of the carbon-lithium bond order is still significant, as evidenced by coupling in methyl-lithium tetramers in ether^{29,30}. Coupling³¹ suggests that the tetramer structure which is perturbed by the basic solvent. A cubic tetramer structure has been discussed^{15,30}. The nature of alkyllithiums in THF has been discussed in terms of localized ionic structures³²⁻³⁴. On the other hand, the nature of alkyllithiums in ether has been interpreted in terms of rapidly exchanging the primary form in preponderance.



Regarding the effect of basic solvents on the structure of organolithium compounds, the group at Syracuse University^{36,37}. Although in detail here, the data indicate that such compounds

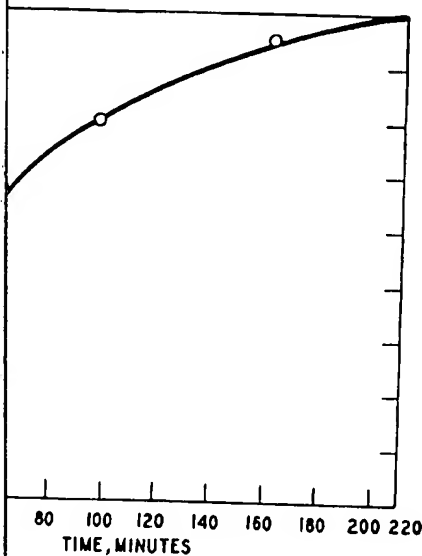
exist as intimate or solvent separated ion pairs, with the former often being present as dimeric (or higher) aggregates. The spectral characteristics of each species have been determined, and the fraction of solvent-separated ion pairs has been shown to be a sensitive function of the solvating power of the medium, the temperature, and the metal and organic ions. Solvent-separated ions are generally more reactive than intimate pairs, although at least one exception to this generalization has been found—namely, the metalation of fluorene by fluorenyllithium in dioxaneglycol ether mixed solvent²⁹.

The addition of stoichiometric quantities of basic compounds to hydrocarbon solutions of alkyllithiums of Group A has been studied, although the results are still rather inconclusive. However, it is clear from the works of Eastham and coworkers that the addition of ethers and amines drastically accelerates chemical reactions of the alkyllithium until the ratio of oxygen or nitrogen to lithium is approximately one-half^{38,39}. The conclusion drawn by Eastham that complexed dimers of *n*-butyllithium are formed by the addition of ether has not been confirmed, however²⁷. Apparently, each tetramer unit of *n*-butyllithium is complexed to two ether units in one form, although others may be present. Other Lewis bases have been observed to change the chemical and physical properties of alkyllithiums. Thus, the accelerating effect of lithium alkoxides on the rates of thermal decomposition of alkyllithiums have been studied by several groups⁴⁰⁻⁴². The effect of lithium *t*-butoxide on the alkylation of naphthalene by *t*-butyllithium has also been observed⁴³. In general, the effect of such basic salts is to accelerate chemical reactions of alkyllithiums. The reason is not entirely clear at this time, although one may speculate that mixed aggregates of the type $\text{Li}_4\text{R}_3\text{OR}$ are more prone to dissociation, providing a higher concentration of reactive species, whether they be monomers or dimers. Early work by Brown and coworkers^{44,45} indicated that the addition of lithium ethoxide (or triethylamine) to ethyllithium in benzene did not fragment the hexameric species. However, it now appears that this is not the general case, and in one instance the break-up of the *sec*-butyllithium tetramers by lithium *sec*-butoxide has been observed⁴⁶. We shall discuss the effect of basic solvents in more detail in a later section.

In summary, we may characterize organolithium compounds as essentially polar covalent compounds which prefer to aggregate through multi-center carbon-lithium bonding, but which may partially dissociate under the influence of basic compounds, or when the organic moiety can conveniently stabilize the high negative charge on the carbon atom in monomer units. We would expect the rates (and stereochemistry) of their reactions to be highly dependent upon the nature of the medium, the substrate, the organic moiety on the lithium compound, and the concentration range employed. In the subsequent sections, we shall investigate the role that each of these factors plays in determining the kinetics and mechanism of some characteristic reactions of lithium alkyls, particularly additions to carbon-carbon double bonds.

III. RATE OF POLYMERIZATION

Rate of polymerization (*R*) represents an over-all rate obtained by measuring the disappearance of monomer in the polymerization reaction when both initiation and propagation reactions are occurring simultaneously. Welch⁴⁰⁵ studied the polymerization of styrene in benzene with *n*-butyllithium. The plot of monomer concentration (or conversion) against time is sigmoidal in shape, an observation agreed too by all the investigators (Figure 2). He assumed that each molecule of *n*-butyllithium initiates one polymer chain, that there is no termination reaction, and that the



Butadiene (1.4 m./l.) in cyclohexane at 50° C with *n*-BuLi.

Butyllithium may be calculated from the degree of polymerization produced. It was reported that the rate of polymerization, the term rate of propagation was used but, under conditions, the initiation step could not have been neglected (reaction) is first order in initial monomer concentration. The effective *n*-butyllithium concentration depending on the latter is greater or less than 0.020*M*. It was reported that the growing chains is prevalent, that the association of the latter is 0.02*M* represents the critical concentration for the polymerization of variable and unknown amounts of impurities in the effective *n*-butyllithium concentration from the initial monomer concentration. The value $\langle DP \rangle$ (degree of polymerization) from the molecular weight-viscosity relationship. However, this relationship is not very satisfactory. The experimental measurements are always present, the relationship is always true, as will be shown later, and Szwarc's measurements are inaccurate by a factor of about 2. In view of these observations, the relationship is viewed with some doubt.

In the polymerization of isoprene in toluene with *n*-BuLi, the rate was substantially what Welch²⁰⁵ found for styrene. The polymerization was first order in monomer over the range 0.03*M*, the rate actually decreased as ethyl-*n*-butyllithium, as did Welch²⁰⁵, explained these observations as due to the inactive polymer-Li aggregate, and the concen-

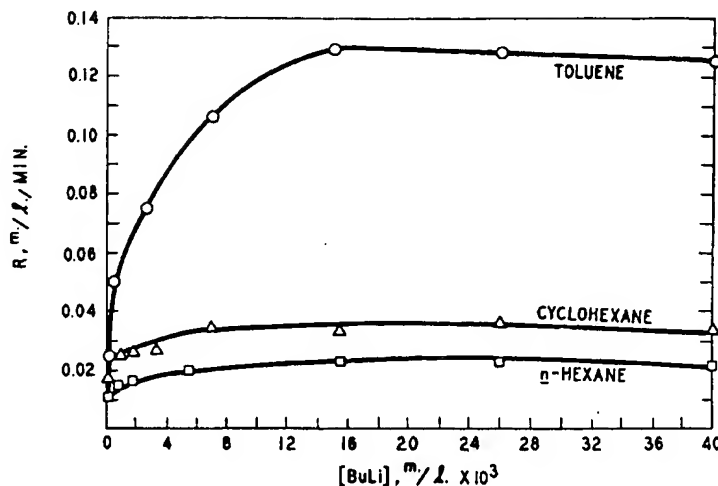


FIG. 3.—Rate of polymerization of butadiene (1.7 m./l.) at 50° C. Reproduced from *J. Polymer Sci. A3*, 153 (1965) with permission of the copyright owner.

tration at which the rate became independent of RLi concentration was considered to be the critical or limiting concentration for association. While there is no doubt that association of the polymer-Li in nonpolar solvent must occur, the idea of "critical" concentration is unsupported by other data.

O'Driscoll and Tobolsky⁴⁸ examined the maximum rate of polymerization of styrene in benzene with *n*-butyllithium and reported that above a certain initial butyllithium concentration, rate was independent of *n*-butyllithium concentration and proportional to the square of the initial monomer concentration, $R = K(M)^2$. The maximum rate was calculated from the linear portion (usually around 10–50% conversion) of the sigmoidal-shaped conversion as a function of time curve. The relationship $R = K(M)^2$ was also reported by others^{49,50} for butadiene, styrene, and isoprene in different hydrocarbon solvents. The pertinent data obtained by these three groups are summarized in Table I. The relationships between R and (*n*-BuLi)₀ and (*M*)₀ are illustrated in Figures 3 to 8.

O'Driscoll and Tobolsky⁴⁸ suggested the following mechanism of polymerization, in which monomeric butyllithium initiates polymerization and termination occurs by association between the propagation anion, the lithium counterion, and another butyllithium:

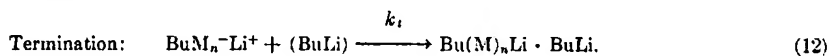
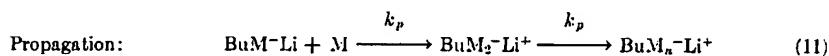
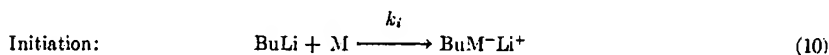
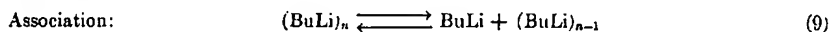


TABLE I

POLYMERIZATION RATE CONSTANT (K) AT QUASI-STATIONARY PERIOD $R = K(M)^2$

Monomer	Solvent	Temp. (°C)	(<i>n</i> -BuLi) ₀ , <i>M</i>	<i>K</i> , liter/mole-min	Ref.
Styrene	Benzene	20	4.2×10^{-3}	0.0235	48
Styrene	Cyclohexane	30	7×10^{-3}	0.0131	50
Isoprene	Hexane	30	1×10^{-3}	0.0036	49
Isoprene	Cyclohexane	30	1×10^{-3}	0.0022	50
Isoprene	Cyclohexane	50	1×10^{-3}	0.0189	50
Isoprene	Hexane	50	1×10^{-3}	0.0148	50
Isoprene	Toluene	50	2×10^{-3} to 4×10^{-3}	0.118	50
Butadiene	Cyclohexane	30	4×10^{-3}	0.0012	50
Butadiene	Cyclohexane	50	4×10^{-3}	0.0114	50
Butadiene	Hexane	50	4×10^{-3}	0.0076	50
Butadiene	Toluene	50	1×10^{-3}	0.0443	50

Making the steady-state assumption for the growing polymer chains, they derived

$$d(\text{Bu}(\text{M})_n\text{Li})/dt = 0 \quad n = 1 \text{ to infinity} \quad (13)$$

$$k_i(\text{M})(\text{BuLi}) = k_t(\text{Bu}(\text{M})_n\text{Li}^+)(\text{BuLi}) \quad (14)$$

$$(\text{Bu}(\text{M})_n\text{Li}^+) = (k_i/k_t)(\text{M}) \quad (15)$$

$$R_p = k_p(\text{Bu}(\text{M})_n\text{Li}^+)(\text{M}) \quad (16)$$

$$= (k_i k_p / k_t)(\text{M})^2 \quad (17)$$

$$= K(\text{M})^2. \quad (18)$$

With what we know today regarding initiation and propagation reactions, the above mechanism cannot be correct. At the time, the authors were unaware of the fact that the maximum rate of polymerization is a measure of both initiation and propagation reactions. New active polymer chains are forming continuously and

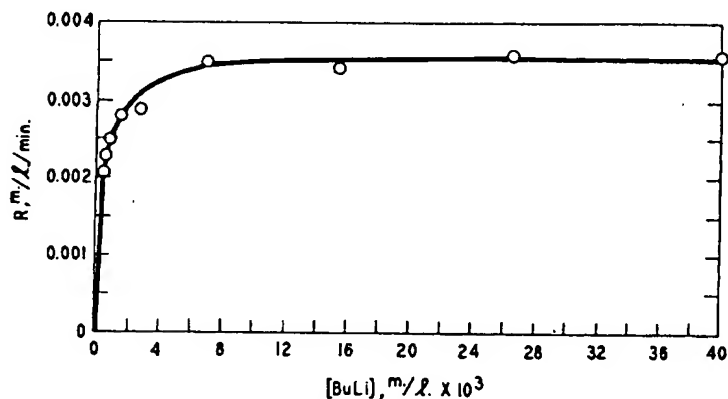


FIG. 4.—Rate of polymerization of butadiene (1.7 m./l.) in cyclohexane at 30° C. Reproduced from *J. Polymer Sci.* A3, 153 (1965) with permission of the copyright owner.

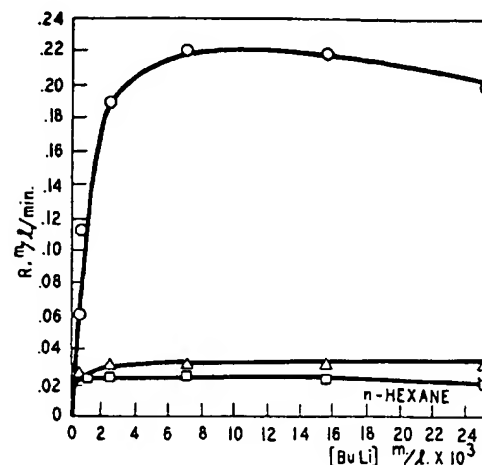


FIG. 5.—Rate of polymerization of isoprene (1.3 m./l.) in *n*-HEXANE. *J. Polymer Sci.* A3, 153 (1965) with permission

simultaneously as propagation is in progress, when is used as the initiator. This fact was established by independently with different methods.

Worsford and Bywater⁵¹ were among the first to butyllithium system that the number of molecule tinuously increasing as the monomer concentration i by simultaneous spectrophotometric analysis for concentrations. Morton, Bostick, and Clarke¹⁶, by viscometric molecular weights of polyisoprene pre lithium, showed that initiation was slow and that not sumed at the end of polymerization. Sinn and Hofn

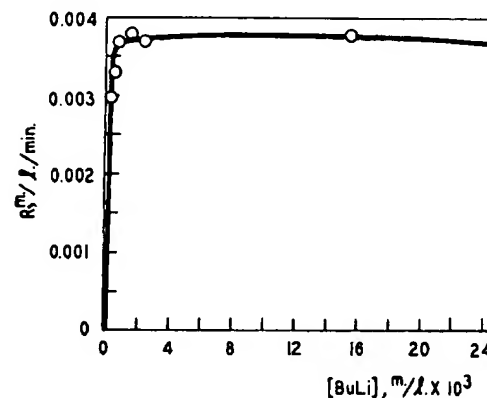


FIG. 6.—Rate of polymerization of isoprene (1.3 m./l.) in *n*-HEXANE. *J. Polymer Sci.* A3, 153 (1965) with p

TABLE I

CONSTANT (K) AT QUASI-STATIONARY PERIOD $R = K(M)^2$

Temp. (°C)	(<i>n</i> -BuLi) ₀ , <i>M</i>	<i>K</i> , liter/mole-min	Ref.
20	4.2×10^{-3}	0.0235	48
30	7×10^{-3}	0.0131	50
30	1×10^{-2}	0.0036	49
30	1×10^{-2}	0.0022	50
50	1×10^{-2}	0.0189	50
50	1×10^{-2}	0.0148	50
50	2×10^{-2} to 4×10^{-2}	0.118	50
30	4×10^{-2}	0.0012	50
50	4×10^{-2}	0.0114	50
50	4×10^{-2}	0.0076	50
50	1×10^{-2}	0.0443	50

umption for the growing polymer chains, they derived

$$d(M_n Li)/dt = 0 \quad n = 1 \text{ to infinity} \quad (13)$$

$$d(BuLi) = k_i(Bu(M)_n^- Li^+)(BuLi) \quad (14)$$

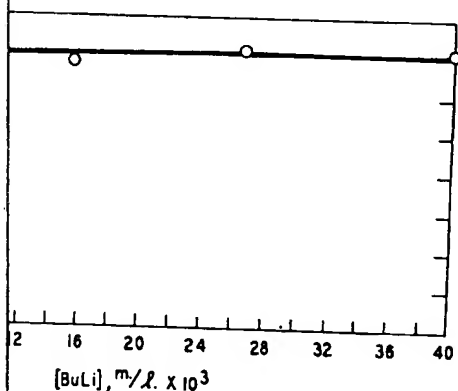
$$Bu(M)_n^- Li^+ = (k_i/k_t)(M) \quad (15)$$

$$R_p = k_p(Bu(M)_n^- Li^+)(M) \quad (16)$$

$$= (k_i k_p/k_t)(M)^2 \quad (17)$$

$$= K(M)^2 \quad (18)$$

regarding initiation and propagation reactions, the correct. At the time, the authors were unaware of the polymerization is a measure of both initiation and active polymer chains are forming continuously and



on of butadiene (1.7 m./l.) in cyclohexane at 30° C. A3, 153 (1965) with permission of the copyright owner.

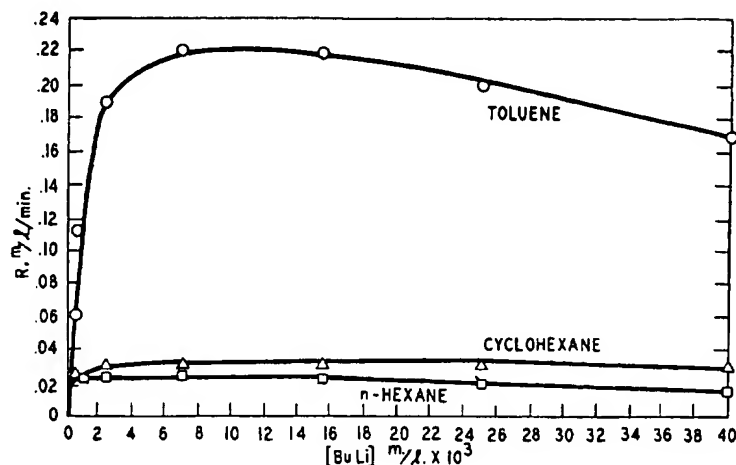


Fig. 5.—Rate of polymerization of isoprene (1.3 m./l.) at 50° C. Reproduced from *J. Polymer Sci. A3*, 153 (1965) with permission of the copyright owner.

simultaneously as propagation is in progress, when ethyllithium or *n*-butyllithium is used as the initiator. This fact was established by a number of investigators quite independently with different methods.

Worsford and Bywater⁵¹ were among the first to show in the styrene-benzene-*n*-butyllithium system that the number of molecules of polystyryllithium is continuously increasing as the monomer concentration is decreasing. This was achieved by simultaneous spectrophotometric analysis for styrene and polystyryl anion concentrations. Morton, Bostick, and Clarke⁵², by comparing the kinetic and the viscometric molecular weights of polyisoprene prepared in hexane with *n*-butyllithium, showed that initiation was slow and that not all of the butyllithium was consumed at the end of polymerization. Sinn and Hofmann⁵² showed that only 33% of

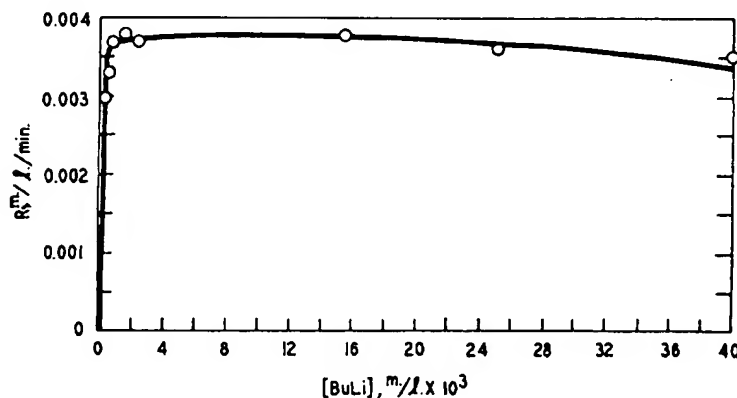


Fig. 6.—Rate of polymerization of isoprene (1.3 m./l.) in cyclohexane at 30° C. Reproduced from *J. Polymer Sci. A3*, 153 (1965) with permission of the copyright owner.

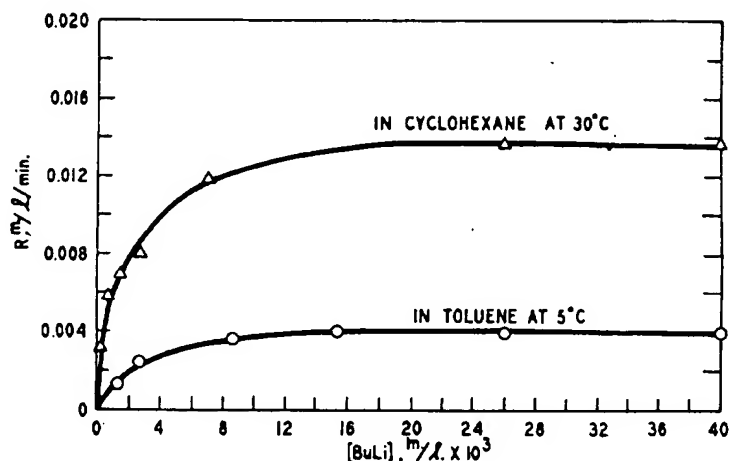


FIG. 7.—Rate of polymerization of styrene (1.0 m./l.). Reproduced from *J. Polymer Sci. A3*, 153 (1965) with permission of the copyright owner.

the initial amount of *n*-butyllithium had reacted at the point where about 70% of the original monomer, isoprene, was polymerized. They determined the concentration of unreacted *n*-butyllithium by measuring the amount of butane generated on hydrolysis of the reaction mixture. Also employing gas chromatographic analysis, Hsieh⁵⁰ examined the relationships between unreacted *n*-butyllithium concentrations and polymer conversion for three different monomers, each at four different initial con-

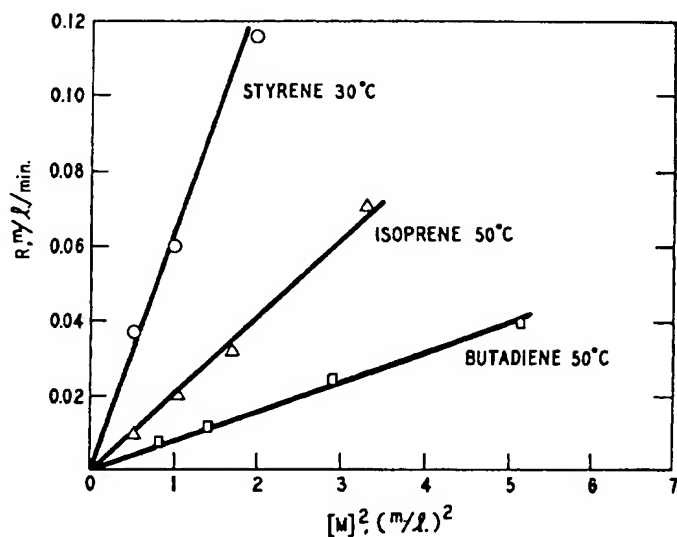


FIG. 8.—Rate of polymerization in cyclohexane versus $[M]^2$. Reproduced from *J. Polymer Sci. A3*, 153 (1965) with permission of the copyright owner.

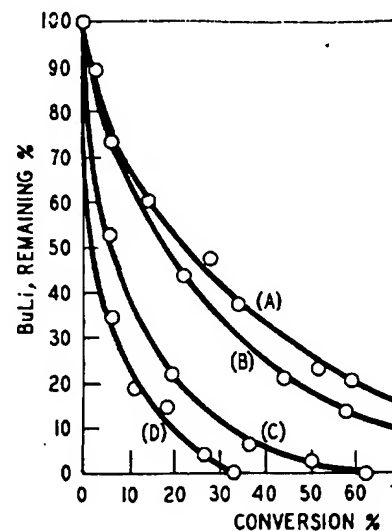


FIG. 9.—Relationship between BuLi remaining and butadiene (1.7 m./l.) in cyclohexane at 50° C: $[n\text{-BuLi}] =$ (A) m./l.; (C) 2.3×10^{-3} m./l.; (D) 0.9×10^{-3} m./l.⁵⁰

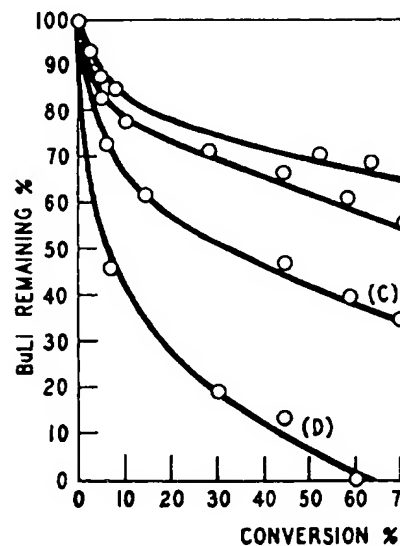
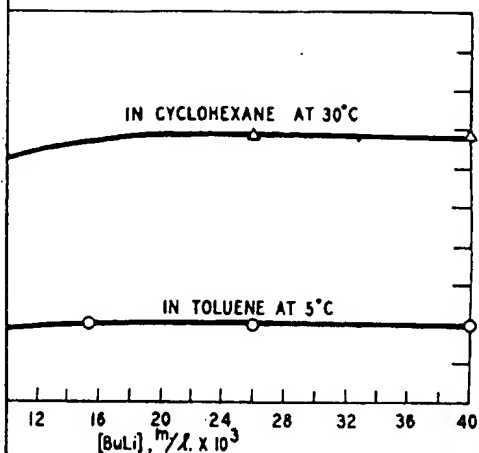
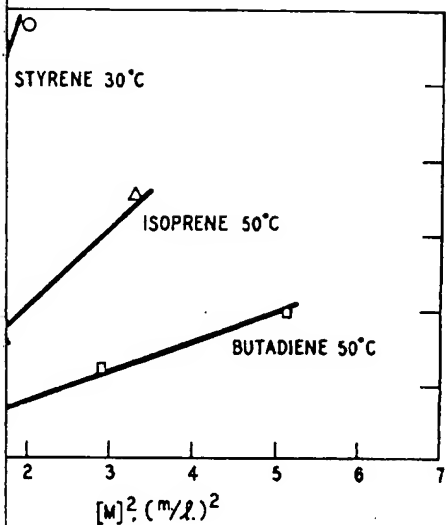


FIG. 10.—Relationship between BuLi remaining and conversion (1.3 m./l.) in cyclohexane at 50° C: $[n\text{-BuLi}] =$ (A) 2.6×10^{-3} m./l.; (C) 2.6×10^{-3} m./l.; (D) 0.9×10^{-3} m./l.⁵⁰



polymerization of styrene (1.0 m./l.). Reproduced from [3] (1965) with permission of the copyright owner.

lithium had reacted at the point where about 70% of the monomer was polymerized. They determined the concentration of unreacted *n*-butyllithium by measuring the amount of butane generated on hydrolysis. Also employing gas chromatographic analysis, Hsieh³⁰ determined the relationship between unreacted *n*-butyllithium concentrations and different monomers, each at four different initial con-



polymerization in cyclohexane versus $[M]^2$. Reproduced from [3] (1965) with permission of the copyright owner.

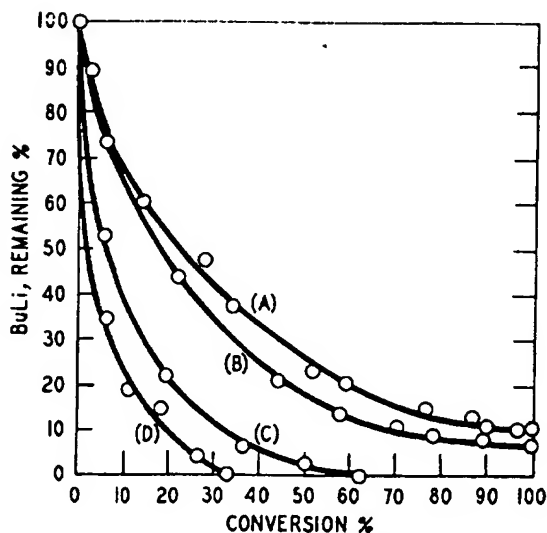


FIG. 9.—Relationship between BuLi remaining and conversion of polymerization of butadiene (1.7 m./l.) in cyclohexane at 50° C: $[n-BuLi]$ = (A) 26×10^{-3} m./l.; (B) 8.7×10^{-3} m./l.; (C) 2.3×10^{-3} m./l.; (D) 0.9×10^{-3} m./l.³⁰

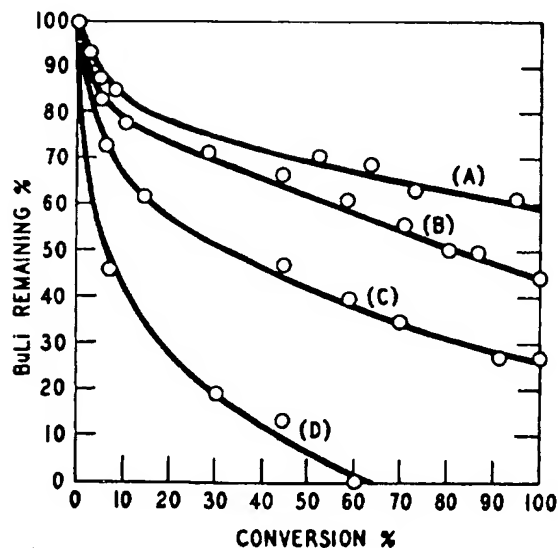


FIG. 10.—Relationship between BuLi remaining and conversion of polymerization of isoprene (1.3 m./l.) in cyclohexane at 50° C: $[n-BuLi]$ = (A) 26×10^{-3} m./l.; (B) 8.7×10^{-3} m./l.; (C) 2.6×10^{-3} m./l.; (D) 0.9×10^{-3} m./l.³⁰

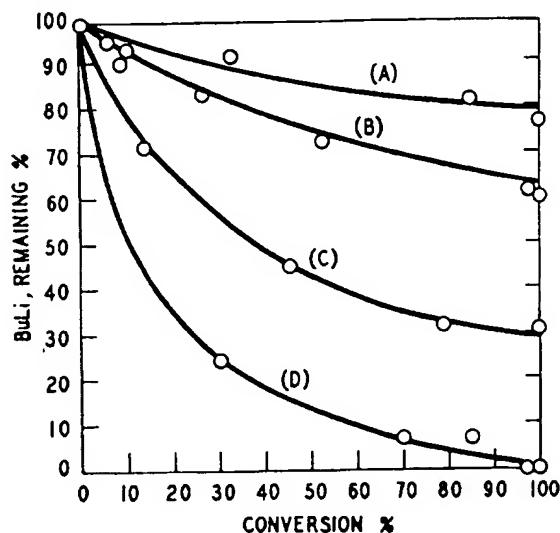


FIG. 11.—Relationship between BuLi remaining and conversion of polymerization of styrene (1.0 m./l.) in cyclohexane at 50° C; $[n\text{-BuLi}] =$ (A) 26×10^{-3} m./l.; (B) 8.7×10^{-3} m./l.; (C) 2.6×10^{-3} m./l.; (D) 0.9×10^{-3} m./l.⁵⁰.

centrations of *n*-butyllithium and in three different solvents. Some of the data are reproduced in Figures 9 to 12.

The curves of conversion as a function of unreacted butyllithium for the three monomers at various butyllithium concentrations clearly demonstrated rate of polymerization *R* to be a combination of rates of propagation and initiation. They also showed that, at higher concentration, proportionally less butyllithium is

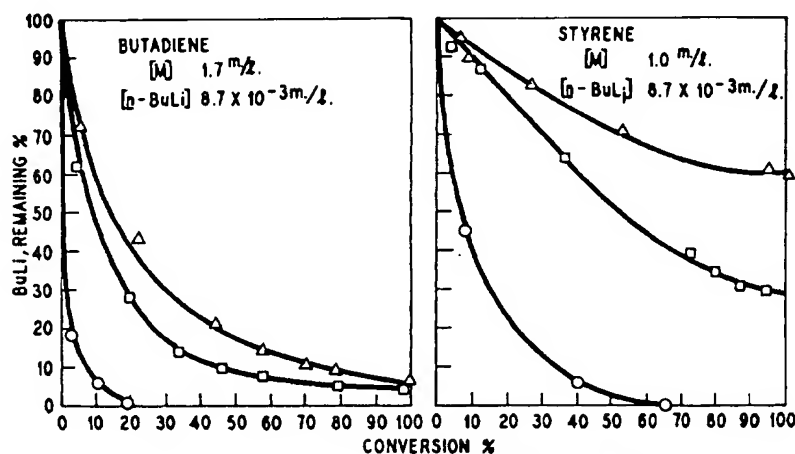


FIG. 12.—Effect of solvent on rate of initiation at 50° C; Δ cyclohexane; \square *n*-hexane; \circ toluene⁵⁰.

consumed. This of course is related to the relative rates which, in turn, are dependent upon a particular set of facts that both rates of initiation and propagation concentration. It was also pointed out⁵⁰ the rate of polymerization increases with temperature increase, because both initiation and propagation rates are affected.

To consider the mechanism of the over-all polymerization, it is not only the self-association of initiator but also the cross-association of initiator with monomer. Morton and his coworkers^{16,53,54} have shown that polyisoprenyllithium form mixed aggregates and that polyisoprenyllithium to form mixed aggregates.



According to Morton, the cross-complex is more favorable than the self-complex, as soon as ethyllithium reacts with isoprene, it ties up some of the ethyllithium in the cross-complex. Morton suggested that the essential reaction is the conversion of ethyl or *n*-butyl into a "*n*" meric polyisoprene mixed association complexes. Consequently, we have a complex system.

Few attempts have been made to study the mechanism of polymerization. Francois, Sinn, and Parrod⁵⁶ studied the propagation of lithium in the presence of excess ethyllithium in increasing amounts of ethyllithium led to retardation of the initiation reaction of *sec*-butyllithium in lithium in heptane, and concluded that the intermediate was quite rapid.

It is clear that the over-all mechanism of polymerization involves dissociation of the initiator molecules, association-dissociation of the mixed addition of monomer units to each of these species. A complex system has not been accomplished at this time.

Jenmer⁵⁸ studied the polymerization of isoprene in high pressure. It was observed that the over-all polymerization rate was high. Presumably both initiation and propagation rates are high. It was also observed that the stereospecificity of butadiene polymerization at high pressure, under pressure, the anionic character of the polymerization was high.

It has been shown⁵⁹⁻⁶¹ that the presence of lithium

TABLE II
MAXIMUM INCREASE IN RATE OF POLYMERIZATION
METAL *tert*-BUTOXIDES⁶²

Monomer	Maximum rate	
	Na	K
Butadiene ^b	8	20
Styrene ^c	25	100

^a In cyclohexane at 30° C.

^b $(Bd)_0 = 1.6$ m./liter, $(BuLi)_0 = 1.55 \times 10^{-3}$ m./liter.

^c $(St)_0 = 0.7$ m./liter, $(BuLi)_0 = 1.26 \times 10^{-3}$ m./liter.

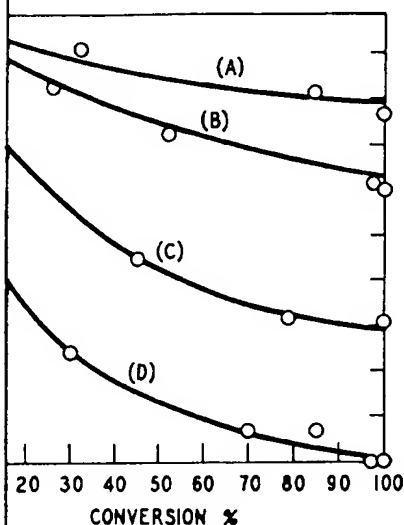


Figure 1. Relationship between BuLi remaining and conversion of polymerization of styrene at 50°C; $[n\text{-BuLi}] = (\text{A}) 26 \times 10^{-3} \text{ m./l.}; (\text{B}) 8.7 \times 10^{-3} \text{ m./l.}; (\text{C}) 0.9 \times 10^{-3} \text{ m./l.}; (\text{D}) 0.1 \times 10^{-3} \text{ m./l.}$

mon and in three different solvents. Some of the data are shown in Figure 1.

As a function of unreacted butyllithium for the three different concentrations clearly demonstrated rate of combination of rates of propagation and initiation. They are, at lower concentration, proportionally less butyllithium is

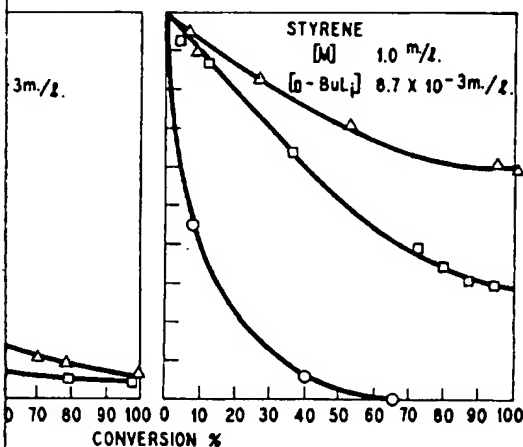


Figure 2. Effect of solvent on rate of initiation at 50°C; Δ cyclohexane; \square n-hexane; \circ toluene¹⁰.

consumed. This of course is related to the relative rates of initiation and propagation which, in turn, are dependent upon a particular monomer-solvent combination. The rate of polymerization is proportional to $(M)^2$. This is in agreement with the facts that both rates of initiation and propagation are proportional to monomer concentration. It was also pointed out⁵⁰ the rate of polymerization increased fourfold per 10°C temperature increase, because both initiation and propagation increased.

To consider the mechanism of the over-all polymerization reaction, one is confronted with not only the self-association of initiator and polymer lithium, but also cross-association. Morton and his coworkers^{16,53,54} showed that butyllithium and polyisoprenyllithium form mixed aggregates and that ethyllithium interacts with polyisoprenyllithium to form mixed aggregates.



According to Morton, the cross-complex is more favored in the above equation which means that, as soon as ethyllithium reacts with isoprene to form M_nLi , the latter can tie up some of the ethyllithium in the cross-complex. Cubbon and Margenson⁵⁵ suggested that the essential reaction is the conversion of the hexameric RLi (where R is ethyl or n -butyl) into a " n " meric polyisoprenyllithium through a series of mixed association complexes. Consequently, we are dealing with an extremely complex system.

Few attempts have been made to study the nature of the cross-complexes. Francois, Sinn, and Parrod⁵⁶ studied the propagation reaction of polyisoprenyllithium in the presence of excess ethyllithium in cyclohexane. The presence of increasing amounts of ethyllithium led to retardation. Roover and Bywater⁵⁷ studied the initiation reaction of *sec*-butyllithium in the presence of polyisoprenyllithium in heptane, and concluded that the intermolecular exchange between the two was quite rapid.

It is clear that the over-all mechanism of polymerization involves association-dissociation of the initiator molecules, association-dissociation of the living polymer molecules, and association-dissociation of the mixed aggregates, as well as possible addition of monomer units to each of these species. A complete treatment of this complex system has not been accomplished at this writing.

Jenner⁵⁸ studied the polymerization of isoprene in heptane with n -butyllithium at high pressure. It was observed that the over-all polymerization rate is accelerated. Presumably both initiation and propagation rates are furthered. The decrease in stereospecificity of butadiene polymerization at high pressure led Jenner to conclude that, under pressure, the anionic character of the polymerization is enhanced.

It has been shown⁵⁹⁻⁶¹ that the presence of lithium *tert*-butoxide generally de-

TABLE II
MAXIMUM INCREASE IN RATE OF POLYMERIZATION BY ASSOCIATION WITH METAL *tert*-BUTOXIDES⁶²

Monomer	Maximum rate increase, fold ^a			
	Na	K	Rb	Cs
Butadiene ^b	8	20	20	7
Styrene ^c	25	100	30	60

^a In cyclohexane at 30°C.

^b $(BD)_0 = 1.6 \text{ m./liter}$, $(BuLi)_0 = 1.55 \times 10^{-3} \text{ m./liter}$.

^c $(S)_0 = 0.7 \text{ m./liter}$, $(BuLi)_0 = 1.26 \times 10^{-3} \text{ m./liter}$.

TABLE III
RELATIVE VINYL UNSATURATION OF POLYBUTADIENES⁶²

M	Vinyl unsaturation, %	
	BuLi/ <i>t</i> -BuOM ^a	RM or M
Li	7-15	6-10
Na	67	65
K	48	45
Rb	55	62
Cs	53	59

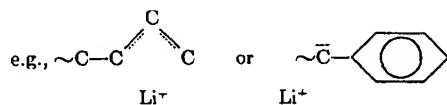
^a Optimum ratio for maximum vinyl unsaturation.

presses the rate of polymerization with *n*-butyllithium. The effects of lithium *tert*-butoxide on initiation and propagation have been studied separately and will be discussed later in the article. Hsieh and Wofford⁶², however, showed that the presence of other alkali-metal alkoxides in the alkyllithium-initiated polymerization drastically increase the rate of polymerization and vinyl unsaturation in polybutadiene. A summary of maximum increase in rate obtained with alkali metal *tert*-butoxides is shown in Table II.

The maximum vinyl unsaturation of polybutadienes prepared with butyllithium alkali metal *t*-butoxide are approximately the same as those in samples prepared with the corresponding alkali-metal or alkali-metal alkyls (Table III). The authors postulated that in the BuLi-*t*-BuOM (where M = Na, K, Rb, and Cs) system, the propagating center is the dynamic equilibrium between carbon-metal bonds and oxygen-metal bonds.

IV. RATE OF PROPAGATION

Polymerizations initiated by alkyllithiums consist of two key steps, initiation and propagation. The former deals with the addition of a monomer to an alkyllithium compound such as butyllithium. The propagation reaction is the growth step which deals with the addition of a monomer to the active polymer chain. While the active polymer chain is an organolithium compound itself, it is not entirely the same as the initiator. Apart from the fact the polymer-lithium can be of very high molecular weight, it is an allyl or benzyllithium compound which is believed by many to exist as a resonance stabilized complex,



(we are concerning ourselves with polydiene and polystyrene here). It is reasonable to expect that the addition of a monomer to the alkyllithium (initiation) and to the resonance stabilized allylic lithium (propagation) do not follow exactly the same course and rate. Indeed, it was shown recently⁶³ that even the stereochemistry of the addition of butadiene is different between the initiation and propagation reactions.

To study the propagation reaction, one must be able to isolate kinetically the propagation step from the initiation step. In other words, the reaction must be carried out in the complete absence of unreacted initiator, and with precisely known

amounts of active polymer chains. Fortunately, it is mentally separated from propagation, and the rate without the complications arising from cross-association is quite true for the study of the initiation reaction.

Generally, three methods had been employed for initiation. One method is the use of "seeded" initiator¹⁴ pre-reacting the monomer with an initiator such as *n*-butyllithium. The "seeding" technique is sometimes questionable because the amount of monomer required is quite large. Another method is the use of a "seeded" initiator by pre-reacting with the monomer is difficult because a large amount of monomer was required. It has been found that the addition of 1 mole of butadiene (the monomer with the most favorable ratio of propagation to initiation) to 0.1 mole of *n*-butyllithium solution contained about 0.07 mole of polybutadiene unreacted *n*-butyllithium. Obviously, much more than all the initiator can be used up. Another method²¹ is the use of an initiator *in situ*. The desired amount of the initiator is determined by measuring the absorption band of the monomer and the anion. When the concentration of the latter reaches that initiation is complete and the propagation rate is many times faster than the initiation rate. In many cases, the completion of initiation step occurs after the monomer had been polymerized, and to perform the propagation step, fresh monomer must be added to the solution. The third method provides an excellent separation of initiation and propagation, the use of *sec*-butyllithium initiator which reacts with the monomer thirty to sixty times faster than *n*-butyllithium. By analysis of the butane after hydrolysis (from which it was concluded that the initiation of butadiene by *sec*-butyllithium was so rapid that the measurement of rate of propagation between 10% to 40% conversion) was indeed a propagation rate. Other investigators^{21,67} later confirmed this method for their studies.

The measurement of propagation kinetics has been found to be independent of original monomer concentration. This relationship is observed for isoprene, and styrene in solvents such as heptane, cyclohexane, and toluene. Figure 13 illustrates the first-order relationship in monomer concentration for propagation for three monomers was found to be first order and for three solvents toluene > cyclohexane > heptane. It has been found to be $\frac{1}{2}$ order in "living" polystyrene. Among these workers, solvents such as toluene, cyclohexane, and heptane were employed, and concentrations ranging from 10^{-2} to 10^{-3} mole/l. Therefore, for styrene one may write with little doubt the following equation:

The $\frac{1}{2}$ -order kinetics of propagation can be explained if the propagation of polystyryllithium occurs, and that unassociated polystyryllithium is at a much faster rate than the dimeric form; thus

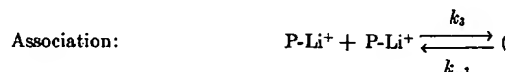


TABLE III

VINYL UNSATURATION OF POLYBUTADIENES⁶²

Vinyl unsaturation, %	
BuLi/t-BuOM ^a	RM or M
7-15	6-10
67	65
48	45
55	62
53	59

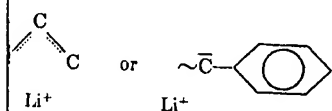
^a in vinyl unsaturation.

polymerization with *n*-butyllithium. The effects of lithium and propagation have been studied separately and will be discussed by Hsieh and Wofford⁶², however, showed that the presence of alkoxides in the alkyllithium-initiated polymerization of polybutadiene and vinyl unsaturation in polybutadiene increase in rate obtained with alkali metal *tert*-butyllithium.

polymerization of polybutadienes prepared with butyllithium is approximately the same as those in samples prepared with alkali or alkali-metal alkyls (Table III). The authors of the *t*-BuOM (where M = Na, K, Rb, and Cs) system, the dynamic equilibrium between carbon-metal bonds and

RATE OF PROPAGATION

polymerizations by alkyllithiums consist of two key steps, initiation and propagation. The addition of a monomer to an alkyllithium compound is the propagation reaction which is the growth step which adds monomer to the active polymer chain. While the active polymer compound itself, it is not entirely the same as the polymer-lithium can be of very high molecular weight compound which is believed by many to exist in solution.



with polydiene and polystyrene here). It is reasonable to assume that the monomer to the alkyllithium (initiation) and to the polymer (propagation) do not follow exactly the same mechanism. It has been shown recently⁶³ that even the stereochemistry of the reaction is different between the initiation and propagation reactions.

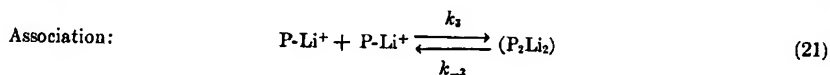
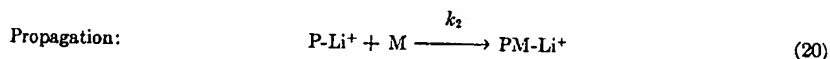
In the propagation reaction, one must be able to isolate kinetically the propagation step. In other words, the reaction must be free of unreacted initiator, and with precisely known

amounts of active polymer chains. Fortunately, the initiation step can be experimentally separated from propagation, and the rate of propagation can be determined without the complications arising from cross-association. Unfortunately, this is not quite true for the study of the initiation reaction, as discussed in another section.

Generally, three methods had been employed for isolating the propagation reaction. One method is the use of "seeded" initiator^{16,53,64,65} which can be prepared by pre-reacting the monomer with an initiator such as ethyllithium or *n*-butyllithium. The "seeding" technique is sometimes questionable. Complete consumption of the initiator by pre-reacting with the monomer is difficult to accomplish, and often a large amount of monomer was required. It has been reported⁶⁶ that by incremental addition of 1 mole of butadiene (the monomer with the lowest propagation rate and, therefore, the most favorable ratio of propagation to initiation rates among the three monomers) to 0.1 mole of *n*-butyllithium in 250 ml cyclohexane, the final solution contained about 0.07 mole of polybutadienyllithium and 0.03 mole of the unreacted *n*-butyllithium. Obviously, much more butadiene must be added before all the initiator can be used up. Another method⁵¹ consists of preparing the "seeded" initiator *in situ*. The desired amount of the initiator is added to the solution containing the monomer and solvent, and the reaction is followed photometrically using the known absorption band of the monomer and the absorption band of the polymer anion. When the concentration of the latter reaches a constant value, it is considered that initiation is complete and the propagation rate is then followed. However, in many cases, the completion of initiation step occurred only after most of the monomer had been polymerized, and to perform the propagation study, one must add fresh monomer to the solution. The third method⁵⁰ is the least cumbersome and provides an excellent separation of initiation and propagation steps. It is based on the use of *sec*-butyllithium initiator which reacts with monomers approximately thirty to sixty times faster than *n*-butyllithium. By employing gas chromatographic analysis of the butane after hydrolysis (from unreacted *sec*-butyllithium), Hsieh⁵⁰ concluded that the initiation of butadiene isoprene, and styrene, with *sec*-butyllithium was so rapid that the measurement of rate of disappearance monomer (usually between 10% to 40% conversion) was indeed the measurement of true propagation rate. Other investigators^{21,67} later confirmed this observation and adopted this method for their studies.

The measurement of propagation kinetics has shown that the reaction is first order in original monomer concentration. This relationship was true for butadiene, isoprene, and styrene in solvents such as heptane, cyclohexane, benzene, and toluene. Figure 13 illustrates the first-order relationship in cyclohexane⁶⁶. The order of rate of propagation for three monomers was found to be styrene > isoprene > butadiene, and for three solvents toluene > cyclohexane > hexane. The propagation reaction has been found to be $\frac{1}{2}$ order in "living" polystyrene by several groups^{16,19,51-53,68,69}. Among these workers, solvents such as toluene, benzene and cyclohexane were employed, and concentrations ranging from 10^{-2} down to $10^{-5} M$ were investigated. Therefore, for styrene one may write with little doubt that $R_p = k_p(RLi)_0^{1/2}(M)_0$.

The $\frac{1}{2}$ -order kinetics of propagation can be explained on the basis that dimerization of polystyryllithium occurs, and that unassociated polystyryllithium propagates at a much faster rate than the dimeric form; thus,



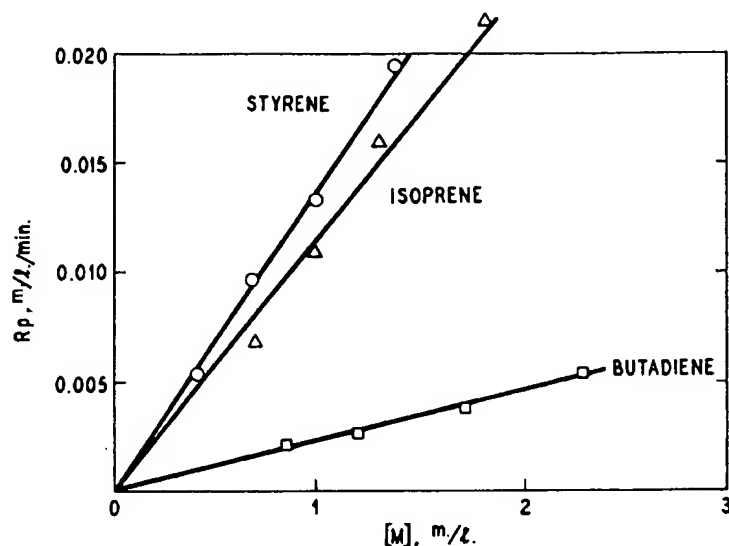


FIG. 13.—Rate of propagation in cyclohexane at 30° C versus $[M]$ (Ref. 66). Reproduced from *J. Polymer Sci. A3*, 173 (1965) with permission of the copyright owner.

where $P-Li^+$ and $PM-Li^+$ are unassociated, active polymer-Li, M is monomer, and (P_2Li_2) is associated polymers. Here k_2 is the propagation rate constant, and k_3 and k_{-3} are forward and reverse constants for the association reaction. From Equation (21),

$$k_3/k_{-3} = (P_2Li_2)/(P-Li^+)^2 = K_3 \quad (22)$$

$$(P_2Li_2) = K_3(P-Li^+)^2. \quad (23)$$

The initial RLi concentration n_0 is

$$n_0 = (P-Li^+) + 2(P_2Li_2), \quad (24)$$

then

$$(P-Li^+) = n_0 - 2(P_2Li_2). \quad (25)$$

From Equations (23) and (25)

$$(P-Li^+) = n_0 - 2K_3(P-Li^+)^2 \quad (26)$$

$$(P-Li^+) = (\frac{1}{2}K_3)[(1 + 8K_3n_0)^{1/2} - 1]. \quad (27)$$

The rate of propagation R_p is

$$-(dM/dt) = k_2(P-Li^+)(M). \quad (28)$$

From Equations (27) and (28)

$$R_p = (k_2/4K_3)(M)[(1 + 8K_3n_0)^{1/2} - 1] \quad (29)$$

This is the general expression for the rate of propagation which can be reduced to

the experimentally observed form by assuming the large)

$$R_p = [k_2/(2K_3)^{1/2}](M)$$

At extremely low initial concentration of alkyllithium press the rate equation by applying the mathematic $1 + mA$. Therefore,

$$R_p = (k_2/4K_3)(M)(4K_3n_0) =$$

The fact that the $\frac{1}{2}$ -order dependence upon initial RLi to concentration as low as about $10^{-5} M$, indicates 10^6 . Such a value of the association constant implies chains are associated in the dimeric form even at lit as $10^{-5} M$.

While several investigators explained the $\frac{1}{2}$ -or dissociation equilibrium, it was the work of Morton first provided the physical evidence for such association of "living" polymers by viscosity (5–20 wt %) solutions resulting from these pol between viscosity (η) and molecular weight (M) is:

$$\eta = KM^{3/4},$$

where K is a constant which included the concentration results obtained from the "living" polymer (PLi) solution, it was shown⁶⁵ that polystyryllithium associated in pairs. Their results are calculated in polystyryllithium in cyclohexane was confirmed by Thus the kinetics and mechanism of the propagation styrene seems to be quite straightforward and well

The kinetics of propagation of polyisoprenyllithium Morton^{16,64}, Spirin⁶⁸, Worsfold and Bywater¹⁸, Hsie and coworkers⁷². Solvents including hexane, heptane and toluene were used in these investigations.

The kinetic orders reported by various workers and can be represented as $\frac{1}{4}$ -order in polyisoprene suggests a degree of association of about 4 for polyisoprene solution⁷³. (Sinn's data show a progressive drop in and the authors concluded that polyisoprenyllithium

TABLE IV
DETERMINATION OF DEGREE OF ASSOCIATION OF
BENZENE SOLUTION AT 25°

Flow time, sec.		
"Living"	"Killed"	$(RLi)_0 \times 10^3 M$
6050	525	5.84
4630	400	2.66
1030	98.1	1.39
825	81.1	1.23
5770	560	0.23

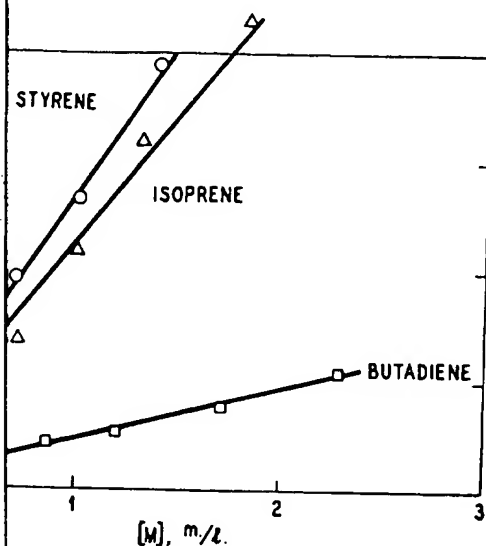


Fig. 3. Propagation in cyclohexane at 30° C versus $[M]$ (Ref. 66).
 Pri. A3, 173 (1965) with permission of the copyright owner.

an unassociated, active polymer-Li, M is monomer, and k_2 is the propagation rate constant, and k_3 and k_4 are constants for the association reaction. From Equation

$$k_3 = (P_2Li_2)/(P-Li^+)^2 = K_3 \quad (22)$$

$$(P_2Li_2) = K_3(P-Li^+)^2 \quad (23)$$

in n_0 is

$$n_0 = (P-Li^+) + 2(P_2Li_2), \quad (24)$$

$$(P-Li^+) = n_0 - 2(P_2Li_2). \quad (25)$$

5)

$$P-Li^+ = n_0 - 2K_3(P-Li^+)^2 \quad (26)$$

$$0 = (\frac{1}{4}K_3)[(1 + 8K_3n_0)^{1/2} - 1]. \quad (27)$$

6)

$$-(dM/dt) = k_2(P-Li^+)(M). \quad (28)$$

8)

$$k_2/4K_3(M)[(1 + 8K_3n_0)^{1/2} - 1] \quad (29)$$

for the rate of propagation which can be reduced to

the experimentally observed form by assuming the term $8K_3n_0$ is large (when n_0 is large)

$$R_p = [k_2/(2K_3)^{1/2}](M)(n_0)^{1/2} \quad (30)$$

At extremely low initial concentration of alkyllithium, $8K_3n_0$ is small. One can express the rate equation by applying the mathematical approximation of $(1 + A)^m = 1 + mA$. Therefore,

$$R_p = (k_2/4K_3)(M)(4K_3n_0) = k_2(M)(n_0). \quad (31)$$

The fact that the $\frac{1}{2}$ -order dependence upon initial RLi concentration, n_0 , is applicable to concentration as low as about $10^{-5} M$, indicates that the value of K_3 is at least 10^6 . Such a value of the association constant implies that 80%-90% of the polymer chains are associated in the dimeric form even at lithium atom concentration as low as $10^{-5} M$.

While several investigators explained the $\frac{1}{2}$ -order kinetics by the association-dissociation equilibrium, it was the work of Morton, Bostick, and Livigni⁶³ which first provided the physical evidence for such association. They determined the degree of association of "living" polymers by viscosity measurements on concentrated (5-20 wt %) solutions resulting from these polymerizations. The relationship between viscosity (η) and molecular weight (M) is given by⁷⁰

$$\eta = KM^{3.4}, \quad (32)$$

where K is a constant which included the concentration term. By comparing the results obtained from the "living" polymer (PLi) solution and the "killed" polymer (PH) solution, it was shown⁶⁵ that polystyryllithium in benzene is almost entirely associated in pairs. Their results are calculated in Table IV. The dimeric nature of polystyryllithium in cyclohexane was confirmed by a light-scattering technique¹⁹. Thus the kinetics and mechanism of the propagation step in the polymerization of styrene seems to be quite straightforward and well worked out.

The kinetics of propagation of polyisoprenyllithium was investigated by Sinn^{17,71}, Morton^{16,64}, Spirin⁶⁸, Worsfold and Bywater¹⁸, Hsieh⁶⁶, and recently by Margerison and coworkers⁷². Solvents including hexane, heptane, cyclohexane, benzene, and toluene were used in these investigations.

The kinetic orders reported by various workers are not significantly different and can be represented as $\frac{1}{4}$ -order in polyisoprenyllithium concentration⁷³. This suggests a degree of association of about 4 for polyisoprenyllithium in hydrocarbon solution⁷³. (Sinn's data show a progressive drop in rate as concentration is reduced and the authors concluded that polyisoprenyllithium molecules exist as hexamer,

TABLE IV
 DETERMINATION OF DEGREE OF ASSOCIATION OF POLYSTYRYLLITHIUM IN
 BENZENE SOLUTION AT 25° C⁶³

Flow time, sec.		$(RLi)_0 \times 10^3 M$	$(S)_0 M$	Association No., n
"Living"	"Killed"			
6050	525	5.84	5.00	2.03
4630	400	2.66	3.90	2.03
1030	98.1	1.39	2.75	1.99
825	81.1	1.23	2.80	1.98
5770	560	0.23	1.75	1.99

TABLE V
ASSOCIATION OF POLYDIENYLITHIUM SPECIES AT 30° C¹⁶

Polymer system	Solvent	(R.I.) ₀ × 10 ³ M	Flow time, sec.		Association No., n
			"Living"	"Killed"	
Polystyrene + isoprene	Benzene	2.4	1924	187.5	1.98
Polystyrene + isoprene	Cyclohexane	2.5	1571	158.4	1.96
	(40° C)				
Polystyrene + butadiene	Benzene	0.60	398.8	38.4	1.99
Polystyrene + butadiene	Cyclohexane	1.6	1171	119	1.97
Polyisoprene	Cyclohexane	0.94	169	16.6	1.98

trimer, and monomer, depending upon the concentration.) By light-scattering measurements in cyclohexane, Worsfold and Bywater¹⁸ obtained an association number of 4. This was confirmed by Sinn¹⁷ in heptane at millimolar concentration by the viscosity method. However, Morton¹⁶ found the association number of 2 (twofold aggregation) for polyisoprenyllithium as well as polybutadienyllithium. Two methods were used, viz., light scattering measurements (*in vacuo*) and viscosity measurements in different solvents, including a "capping" technique. In the latter, a normal polymerization of styrene in a solvent is carried to completion, the viscosity of the solution measured while the polymer is still "living," and then the active chains are "capped" by the addition of 1% to 2% additional isoprene or butadiene. Since it is known⁷⁴ that polystyryllithium reacts very rapidly with these monomers, this method assures the complete conversion of the polystyryllithium into polydiényllithium. Any differences in degree of association between these "living" polymers would thus become immediately apparent by a sharp change in viscosity of the solutions. Their results are summarized in Tables V and VI. Morton's data unequivocally showed that the propagating chains are associated in pairs regardless of the monomer or solvent used.

Thus, two association numbers (2 and 4) have been reported for polyisoprenyllithium. Both numbers were determined from the viscosity method as well as light-scattering measurements. The discrepancy, therefore, cannot be attributed to the experimental methods, nor does it seem likely that it is the result of the choice of solvents. Nevertheless, the genuine difference exists, and a careful re-examination is warranted.

If polyisoprenyllithium molecules are indeed mostly tetrameric in solution, then the $\frac{1}{2}$ -kinetic order can be readily explained utilizing the association-dissociation equilibrium and assuming that only the dissociated molecules propagate. If, on the other hand, the association number is 2, then we are forced to conclude that there is no general correlation between the kinetic order of these polymerizations and the

TABLE VI
LIGHT SCATTERING OF POLYISOPRENYLLITHIUM IN HEXANE AT 27° C¹⁶

Polymer No.	Molecular weight ($M_w \times 10^{-4}$)	
	"Living"	"Killed"
1	3.0	1.5
2	2.6	1.3
	2.6	1.3

state of association of the propagating chain ends. Kinetics for isoprene cannot be readily explained at

The propagation step of butadiene polymerization^{65,75} in cyclohexane by Johnson and Worsfold¹ in cyclohexane and toluene by Hsieh⁶⁶. The results of the $\frac{1}{2}$ ^{19,68,75}, $\frac{1}{4}$ ¹⁶ and $\frac{1}{2}$ ^{66,53,64} power of polybutadiene most plausible explanation for the differences observed by same group at different times^{16,53,64} is that the presence of trace amounts of slow reacting imp

Even though it is not possible to state definitely the propagation, it is reasonably sure that the rate is $\frac{1}{2}$ and $\frac{1}{4}$. This is not consistent with the reported¹⁶ question has been raised⁷³ as to whether the kinetic provide more reliable information about the degree (unfortunately there are no data available for light scattering measurements). It seems to us that both unintentional termination and complexing with lithium both have equally troublesome experimental problems. By summing the $\frac{1}{2}$ order is correct, then we can conclude that the molecules are more heavily associated than those of tetrameric according to his data. He pointed out that *n*-butyllithium (hexamer) and *tert*-butyllithium (tetramer) effects. The real question is whether one can transform order directly to the association number at opinion that the association number does not necessarily kinetic order of the reaction, and concluded that the dienes does not involve a simple association-dissociation mechanism is valid for styrene. One may even speculate that the monomer complexes with the unpolymerized before dissociation and addition occur. It is essentially chemical and physical nature of these aggregates, monomers. Meanwhile, the exact mechanism of the

The determination of absolute rate constants of Sinn^{17,71}, Morton^{16,65} and Francois, Sinn, and Parrott⁷² of isoprene down to concentration of 5×10^{-7} M of the propagation reaction is concentration dependent at polyisoprenyllithium concentrations below 10^{-4} M the rate was first order, and it follows that at 10^{-4} M isoprenyllithium molecules are monomeric and activation range, the observed rate constant is also the absolute rate constant. In heptane was reported to be 0.65 liter/(mole-sec) at Sinn's data showed a continuous increase in reaction order and reached second order at 5×10^{-7} M. A was proposed⁷⁶ to account for the change of kinetic order despite the elaborate precautions taken by Sinn and others, one is still skeptical about the accuracy of the concentrations (10^{-6} to 10^{-7} M). Salts formed from impurities could depress the rates at low concentrations, changing reaction order with concentration. The association, polyisoprenyllithium molecules are in a dissociated form needs more critical examination.

TABLE V

OF POLYDIENYLLITHIUM SPECIES AT 30° C¹⁶

Solvent	(RLI) ₀ × 10 ³ M	Flow time, sec.		Association No., <i>n</i>
		"Living"	"Killed"	
benzene	2.4	1924	187.5	1.98
cyclohexane	2.5	1571	158.4	1.96
(40° C)				
benzene	0.60	398.8	38.4	1.99
cyclohexane	1.6	1171	119	1.97
cyclohexane	0.94	169	16.6	1.98

depending upon the concentration.) By light-scattering alone, Worsfold and Bywater¹⁸ obtained an association number of 2 for polyisoprenyllithium at millimolar concentration by the method of Sinn¹⁷ in heptane at millimolar concentration by the method of Morton¹⁶ found the association number of 2 for polyisoprenyllithium as well as polybutadienyllithium. By light scattering measurements (*in vacuo*) and viscosity measurements, including a "capping" technique. In the latter, styrene in a solvent is carried to completion, the viscometer while the polymer is still "living," and then the active addition of 1% to 2% additional isoprene or butadiene. Polyisoprenyllithium reacts very rapidly with these monomers, complete conversion of the polystyryllithium into polyisoprenyllithium in degree of association between these "living" species is immediately apparent by a sharp change in viscosity. The data are summarized in Tables V and VI. Morton's data indicate the propagating chains are associated in pairs regardless of the solvent used.

Numbers (2 and 4) have been reported for polyisoprenyllithium determined from the viscosity method as well as light scattering. The discrepancy, therefore, cannot be attributed to the method. It seems likely that it is the result of the choice of the solvent. If a genuine difference exists, and a careful re-examination is

made, it is likely that the molecules are indeed mostly tetrameric in solution, then the association number can be readily explained utilizing the association-dissociation equilibrium. If only the dissociated molecules propagate. If, on the other hand, the association number is 2, then we are forced to conclude that there is a genuine difference in the kinetic order of these polymerizations and the

state of association of the propagating chain ends. The significance of the $\frac{1}{2}$ -order kinetics for isoprene cannot be readily explained at this time.

The propagation step of butadiene polymerization was studied in heptane by Spirin^{65,75}, in cyclohexane by Johnson and Worsfold¹⁹, in hexane by Morton^{16,53,64} and in cyclohexane and toluene by Hsieh⁶⁶. The results lead to a rate equation involving the $\frac{1}{2}$ ^{19,68,75}, $\frac{1}{4}$ ¹⁶ and $\frac{1}{3}$ ^{65,53,64} power of polybutadienyllithium concentration. The most plausible explanation for the differences observed by different workers or even by same group at different times^{16,53,64} is that the system can easily be affected by the presence of trace amounts of slow reacting impurities or lithium salts.

Even though it is not possible to state definitely the kinetic order of the butadiene propagation, it is reasonably sure that the rate is of low order, somewhere between $\frac{1}{2}$ and $\frac{1}{4}$. This is not consistent with the reported¹⁶ association number of 2. The question has been raised⁷³ as to whether the kinetic studies or the viscometric data provide more reliable information about the degree of association of living polymer (unfortunately there are no data available for polybutadienyllithium by light-scattering measurements). It seems to us that both would be extremely sensitive to unintentional termination and complexing with lithium salts such as alkoxide, and both have equally troublesome experimental problems. It is difficult to say which method is more likely to give erroneous results. Bywater⁷³ suggested that if we assume the $\frac{1}{2}$ order is correct, then we can conclude that polybutadienyllithium molecules are more heavily associated than those of polyisoprenyllithium, which is tetrameric according to his data. He pointed out that a similar difference between *n*-butyllithium (hexamer) and *tert*-butyllithium (tetramer) may be ascribed to steric effects. The real question is whether one can translate the experimentally determined order directly to the association number at all. Morton¹⁶ has expressed the opinion that the association number does not necessarily bear any relation to the kinetic order of the reaction, and concluded that the propagation reaction of these dienes does not involve a simple association-dissociation equilibrium, even if such a mechanism is valid for styrene. One may even speculate in the case of diene polymerization that the monomer complexes with the unreactive polydienyllithium dimer before dissociation and addition occur. It is essential for us to learn more about the chemical and physical nature of these aggregates, and their interaction with the monomers. Meanwhile, the exact mechanism of these reactions remains uncertain.

The determination of absolute rate constants of propagation was reported by Sinn^{17,71}, Morton^{16,65} and Francois, Sinn, and Parrod⁶⁶. Sinn studied the polymerization of isoprene down to concentration of 5×10^{-7} M. It was found that the order of the propagation reaction is concentration dependent and increases progressively at polyisoprenyllithium concentrations below 10^{-4} M. At concentration of 5×10^{-6} M the rate was first order, and it follows that at this concentration all the polyisoprenyllithium molecules are monomeric and active. Therefore, at this concentration range, the observed rate constant is also the absolute rate constant. The value in heptane was reported to be 0.65 liter/(mole-sec) at 20° C. It is worth noting that Sinn's data showed a continuous increase in reaction order as concentration was lowered and reached second order at 5×10^{-7} M. A rather complicated mechanism was proposed⁷⁶ to account for the change of kinetic order below 5×10^{-7} M. In spite of the elaborate precautions taken by Sinn to ascertain the absence of impurities, one is still skeptical about the accuracy of the rate determinations at such low concentrations (10^{-6} to 10^{-7} M). Salts formed from the destruction of initiator by impurities could depress the rates at low concentrations and give the appearance of changing reaction order with concentration. The assumption that, at 5×10^{-6} M concentration, polyisoprenyllithium molecules are present almost exclusively in dissociated form needs more critical examination.

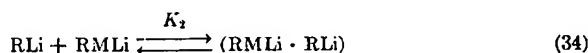
TABLE VI

OF POLYISOPRENYLLITHIUM IN HEXANE AT 27° C¹⁶

No.	Molecular weight ($M_w \times 10^{-3}$)	
	"Living"	"Killed"
	3.0	1.5
	2.6	1.3
	2.6	1.3

Morton^{16,20} determined the degree of association independently from viscosity measurements of the concentrated solutions of the "living" and "killed" polymers. From this the equilibrium constant was calculated and hence the absolute propagation rate constant. It was found that the absolute rate constant was 4.7 liter/(mole-sec) for isoprene at 30° C in hexane. This method is theoretically sound, but its accuracy is somewhat limited. A very small error in the determination of association number can introduce a very large error in the final calculation, since the value of the equilibrium constant is derived from a minute deviation of association number from the limiting value of 2.00.

Francois, Sinn, and Parrod¹⁶ attempted to determine the absolute rate constant of propagation of polyisoprenyllithium in cyclohexane. The reaction was studied in the presence of variable amounts of ethyllithium, which was found to depress the propagation rate. The authors proposed the following reaction scheme and assumed that under all conditions only the unassociated polyisoprenyllithium RMLi, and the mixed dimer RMLi·RLi, exist in appreciable concentrations.



By obtaining rates at various relative concentrations of RMLi and RLi, K_2 and k_p can be determined. The reported value of k_p is about 1.8 liter/(mole-sec). This method represents a very ingenious approach, but the proposed reaction scheme is probably incorrect. In a polymerization system where both polymer-lithium and alkyl lithium exist, the equilibria involved are undoubtedly much more complex. Therefore, while the numerical data obtained fit their mathematical prediction, it is doubtful that the rate constants are true values.

From the above discussion, one can see that the determination of absolute propagation rate constants is extremely difficult. Theoretical and practical problems are significant and much more work is needed in this area.

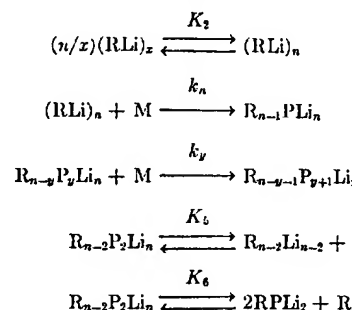
V. RATE OF INITIATION

While the measurement of propagation in the absence of initiation is often possible, as discussed in the previous section, the opposite (*i.e.*, the measurement of initiation rates in the absence of the propagation reaction) is not so easily accomplished. In practice, two methods have evolved to measure initiation rates, namely, the measurement of the decrease in initiator level, usually by determining the amount of hydrocarbon produced by hydrolysis of the alkyl lithium compound⁵²; or, alternatively, by the spectrophotometric measurement of the increase in polymer lithium⁵¹. If the initiation reaction were simply



either of these methods indeed would represent an accurate determination of the rate of this reaction. In fact, the sequence of reactions which occur upon mixing an initiator and an active monomer are much more complex, and the kinetic treatment is correspondingly difficult. In alkyl lithium-initiated systems, the initiator, as well as the adduct, exists as an aggregated species. Moreover, rates of propagation are

often as fast, or faster, than initiation rates. The result of mixing, one is observing a combination of initiation involving a highly complex mixture of initiator and polymer with various degrees of association. To illustrate the problem of initial rates, let us examine the possible reactions of monomer (M) plus alkyl lithium (RLi)_n:

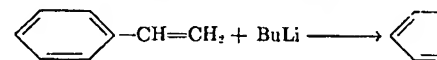


The measured rate of disappearance of RLi, or the rate of appearance of PLi, is then a combination of the rates of Equations (33) and (34) addition steps involving various mixed complexes in

$$-d''(\text{RLi})''/dt = d''(\text{PLi})''/dt = \sum_{n=1}^{\infty} k_n (\text{RLi})_n (\text{M}) + \sum_{y=1}^{\infty} k_y (\text{R}_{n-2}\text{P}_y\text{Li}_n)$$

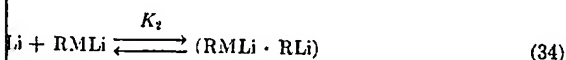
where "RLi" and "PLi" represent the total concentration of lithium in whatever level of complexation and association. Equations (33), (34), and (41) represent only three of the possible dissociations in the system. It is clear that the relative reactivity of each of the species which are involved in such equilibria, the rates of reactions (37), (40), and (41), as compared to the rates of propagation reactions, should markedly influence the kinetic rates should be a function of the solvent and the nature of the monomer. The net result will be a highly complicated kinetic picture which can only be approached by the most simplifying approximations. It is perhaps in work in this area that systems originally chosen for such approximate treatments, and that more complex systems, are better suited for later study. It is the purpose of the remainder of this section to discuss some of the treatments of "initiation rates" which have been made, and to draw some of the conclusions therein.

The first detailed kinetic analysis of an alkyl lithium-initiated system was made by Worsfold and Bywater⁵¹, who studied the reaction in benzene. These workers improved on the earlier work of Tobolsky⁴⁸ and Welch²⁰⁵ by observing the increase in absorption of the benzyl-like lithium compound:



the degree of association independently from viscosity entrained solutions of the "living" and "killed" polymers. A constant was calculated and hence the absolute propagation constant was found that the absolute rate constant was 4.7 liter/30° C in hexane. This method is theoretically sound, but limited. A very small error in the determination of association is a very large error in the final calculation, since the value is derived from a minute deviation of association number 2.00.

Prod⁵⁶ attempted to determine the absolute rate constant of polyisoprenyllithium in cyclohexane. The reaction was studied in amounts of ethyllithium, which was found to depress the rates proposed the following reaction scheme and assumed only the unassociated polyisoprenyllithium $RMLi$, and Li , exist in appreciable concentrations.



various relative concentrations of $RMLi$ and RLi , K_2 and reported value of k_p is about 1.8 liter/(mole-sec). This ingenious approach, but the proposed reaction scheme is a polymerization system where both polymer-lithium and equilibria involved are undoubtedly much more complex. The data obtained fit their mathematical prediction, it is assumed that the constants are true values.

In conclusion, one can see that the determination of absolute rates is extremely difficult. Theoretical and practical problems are involved and more work is needed in this area.

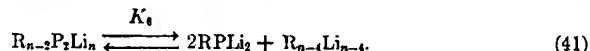
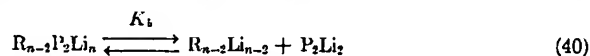
V. RATE OF INITIATION

In the absence of propagation in the absence of initiation is often possible. In the previous section, the opposite (i.e., the measurement of the rate of the propagation reaction) is not so easily accomplished. Various methods have evolved to measure initiation rates, namely, the decrease in initiator level, usually by determining the rate of decrease by hydrolysis of the alkyllithium compound⁵²; or, the photometric measurement of the increase in polymerization rate were simply



Indeed would represent an accurate determination of the rate of the sequence of reactions which occur upon mixing an initiator and monomer are much more complex, and the kinetic treatment is complicated. In alkyllithium-initiated systems, the initiator, as well as the aggregated species. Moreover, rates of propagation are

often as fast, or faster, than initiation rates. The result is that very soon after mixing, one is observing a combination of initiation and propagation reactions involving a highly complex mixture of initiator and polymer lithium compounds, in various degrees of association. To illustrate the problem of interpreting so-called initial rates, let us examine the possible reactions which may occur in the system monomer (M) plus alkyllithium $(RLi)_n$:

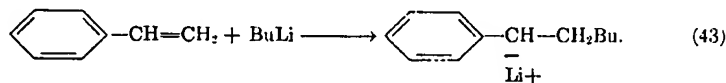


The measured rate of disappearance of RLi , or the rate of appearance of adduct, PLi , is then a combination of the rates of Equations (38) and (39), and other possible addition steps involving various mixed complexes in various levels of aggregation:

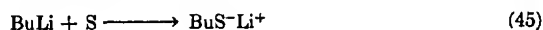
$$-d''(RLi)/dt = d''(PLi)/dt = \sum_{n=1}^{\infty} k_n (RLi)_n (M) + \sum_{y=1}^{\infty} k_y (R_{n-y}P_yLi_n) (M) + \dots \quad (42)$$

where " RLi " and " PLi " represent the total concentration of initiator and polymer lithium in whatever level of complexation and association. Equilibria (37), (40), and (41) represent only three of the possible dissociative reactions which may occur in the system. It is clear that the relative reactivity (toward addition of monomer) of each of the species which are involved in such equilibria may be different. Thus, the rates of reactions (37), (40), and (41), as compared to the addition and propagation reactions, should markedly influence the kinetic pattern of the system. Such rates should be a function of the solvent and the nature of the initiator and adduct. The net result will be a highly complicated kinetic picture which may be solved only by the most simplifying approximations. It is perhaps fortunate for those involved in work in this area that systems originally chosen for investigation were amenable to such approximate treatments, and that more complex systems were deferred for later study. It is the purpose of the remainder of this section, then, to examine what treatments of "initiation rates" have been made, and further to examine the validity of the conclusions therein.

The first detailed kinetic analysis of an alkyllithium-initiated polymerization was made by Worsfold and Bywater⁵¹, who studied the *n*-butyllithium-styrene reaction in benzene. These workers improved on the earlier efforts of O'Driscoll and Tobolsky⁴⁸ and Welch²⁹⁵ by observing the increase in absorbance at 334 mμ due to the formation of the benzyl-like lithium compound:



The authors assumed that absorbance at this wavelength was due only to polystyryl anion, regardless of its state of aggregation, and thereby were able to separate the initiation step from the propagation step. A plot of this "effective" initiator rate as a function of initial *n*-BuLi concentration on a log-log basis yielded a straight line with slope of 0.155 ± 0.016 , provided points taken below $10^{-4} M$ BuLi were eliminated. The order with respect to styrene was determined to be first. Worsfold and Bywater interpreted these data in terms of a simple dissociative mechanism involving initiation exclusively by monomeric butyllithium:



where S and BuS^-Li^+ represent styrene monomer and benzyl lithium adduct respectively. Implicit in their analysis were the assumptions that equilibria such as shown in Equations (40) and (41) do not affect Equation (36) and that once the species BuS^-Li^+ was formed, its participation in such equilibria did not affect the reaction kinetics. Subsequent studies⁷⁷ have verified the $\frac{1}{2}$ -order kinetics of styrene initiation with respect to *n*-butyllithium concentration in toluene solution. The independent determination of the sixfold association of *n*-butyllithium in benzene⁷⁸ adds weight to the interpretation of the kinetics by the use of Equations (44) and (45). Moreover, polymerization of the same monomer with *sec*-butyllithium in benzene²¹ exhibits $\frac{1}{2}$ -order kinetics with respect to initiator, which was found to be fourfold associated in that solvent. In the same paper, initiation rates for the system *sec*-butyllithium-isoprene-benzene were reported, and again the order with respect to initiator was found to be $\frac{1}{2}$. Thus, the data presently available from aromatic hydrocarbon solvents, with two monomers and two initiators tested, may reasonably be interpreted in terms of the dissociative mechanism in which the monomer is the only significantly active species. The absence of any physical data confirming the existence of alkyllithium monomers under these conditions admittedly is

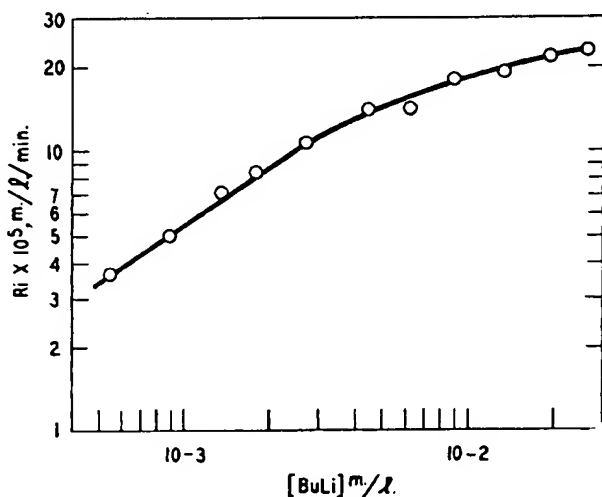


Fig. 14.—Rate of initiation of butadiene (1.6 m./l.) in toluene at 5° C with *n*-BuLi (Ref. 82).

a disturbing element, and has been discussed in so and Worsfold²¹ have objected to some of the arguments. It is apparent that more data are needed, particularly monomer (and dimer) formation. We should also be required, there being too few cases documented which fit the experimental data. Other systems studied in addition to 1,1-diphenylethylene of *n*-butyllithium in benzene. Kinetic studies in basic solvents which will be discussed in a later section. Other studies have dissociative mechanism involving reactive monomer. These include the coupling reaction of ethyllithium and the thermal decomposition of *sec*-butyllithium⁴¹, of *n*-lithium⁴², as well as the alkylation of naphthalene more pertinent, recent results by Hsieh⁸² on the system toluene shows curvature (Figure 14) in a plot of $(\text{BuLi})_2$ with a change from approximately first order to second order range employed. The reasons for the difference between systems in aromatic hydrocarbons is not clear.

It is apparent that a viable alternative mechanism for olefin addition reactions. Despite the objections raised, such an alternative has not been offered at this writing.

If the mechanism of the initiation reaction in aromatic solvents may be classified as follows: observes two differences between vinyl and diene polymer systems, as pertains to the initiation step. First, reaction in aromatic solvents, often as much as 2000 times faster

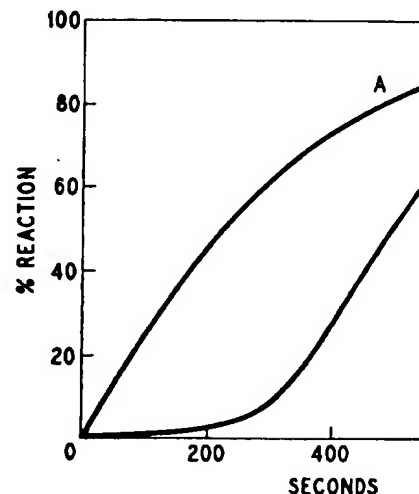
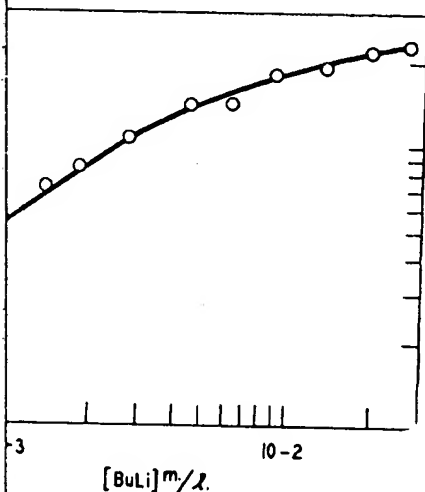


Fig. 15.—Typical curves for the appearance of the active species. A, Reaction of $1.09 \times 10^{-3} M$ *sec*-butyllithium with 5. solution at 30°. B, Reaction of $1.34 \times 10^{-3} M$ *sec*-butyllithium in cyclohexane solution at 40° (Ref. 21). Reproduced from with permission of the copyright owner.

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Initiation of butadiene (1.6 m./l.) in toluene
at 5° C with *n*-BuLi (Ref. 82).

a disturbing element, and has been discussed in some detail by Brown²³. Bywater and Worsfold²¹ have objected to some of the arguments used by Brown, particularly the use of a heat of 37 kcal/mole for the dissociation of the dimer to the monomer¹⁶. It is apparent that more data are needed, particularly regarding the energetics of monomer (and dimer) formation. We should also mention that more kinetic data are required, there being too few cases documented in which the dissociative mechanism fits the experimental data. Other systems studied which do fit include the addition to 1,1-diphenylethylene of *n*-butyllithium⁷⁹ and *tert*-butyllithium⁸⁰, both in benzene. Kinetic studies in basic solvents which fit the dissociative mechanism will be discussed in a later section. Other studies have been reported in which the dissociative mechanism involving reactive monomer is apparently not operative. These include the coupling reaction of ethyllithium and benzyl chloride in benzene⁸¹, the thermal decomposition of *sec*-butyllithium⁴¹, of *n*-butyllithium⁴⁰, and of *t*-butyllithium⁴², as well as the alkylation of naphthalene with *t*-butyllithium⁴³. Perhaps more pertinent, recent results by Hsieh⁸² on the system *n*-butyllithium-butadiene-toluene shows curvature (Figure 14) in a plot of initiation rate as a function of (BuLi) with a change from approximately first order to $\frac{1}{2}$ order over the concentration range employed. The reasons for the difference observed between this and other systems in aromatic hydrocarbons is not clear.

It is apparent that a viable alternative mechanism is needed, especially for olefin addition reactions. Despite the objections raised to the dissociative mechanism, such an alternative has not been offered at this writing.

If the mechanism of the initiation reaction in aromatic solvents is still debatable, the situation in aliphatic solvents may be classified as chaotic. Experimentally one observes two differences between vinyl and diene polymerizations in the two solvent systems, as pertains to the initiation step. First, reactions are quite a bit faster in aromatic solvents, often as much as 2000 times faster than in aliphatic solvents^{21,32,83};

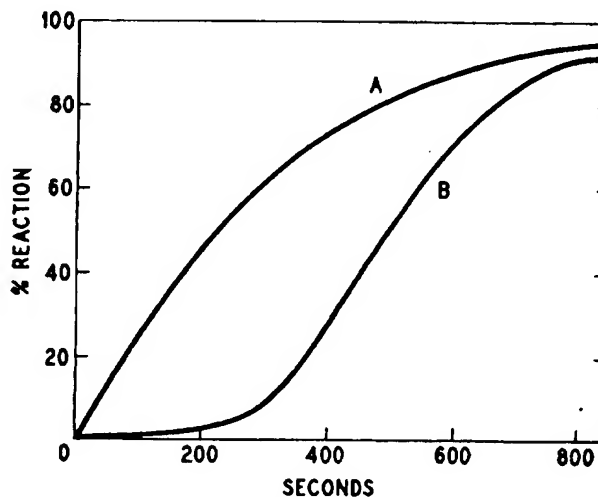
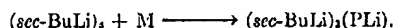


FIG. 15.—Typical curves for the appearance of the uv absorption of polystyryllithium. A, Reaction of $1.09 \times 10^{-3} M$ *sec*-butyllithium with $5.33 \times 10^{-4} M$ styrene in benzene solution at 30°. B, Reaction of $1.34 \times 10^{-3} M$ *sec*-butyllithium with $8.67 \times 10^{-4} M$ styrene in cyclohexane solution at 40° (Ref. 21). Reproduced from *J. Organometal. Chem.* 10, 1 (1967) with permission of the copyright owner.

Second, the rate of appearance of polymer lithium is a sigmoidal function with time as shown in Figure 15 for the system *sec*-butyllithium-styrene-cyclohexane. Various workers have obtained similar data for the systems *n*-BuLi-butadiene-cyclohexane¹⁹, *n*-butyllithium-isoprene-cyclohexane¹⁸, and *sec*-butyllithium-isoprene-*n*-hexane⁶⁰. Initial rates determined during the slow induction period indicate first-order kinetics with respect to both (*sec*-BuLi)₄ and isoprene⁸². Similar kinetic orders were obtained for initial rates in the system *n*-butyllithium-styrene-cyclohexane²¹. Other workers have measured kinetic orders at the period of maximum rate^{18,19,32,82,83}, a region which the system has become very complicated. The kinetic orders in this region run about 0.6–1.4, but little significance has been attached to this value. Generally, the maximum "initiation" rate is proportional to monomer concentration. Moreover, the cause of the initial induction period is unknown at this time. Bywater and coworkers^{21,60} have indicated the primary process to be a direct reaction between monomer and *sec*-butyllithium tetramer to yield a mixed aggregate species:



As discussed above, the reactions which might follow this initial step could be of several types as shown in Equations (39), (40), and (41). It has been pointed out⁶⁰ that an alternate process involving a rate-determining dissociation of the (*sec*-BuLi)₄ to reactive monomer predict first order kinetics in (*sec*-BuLi)₄, but would also lead to zero order in monomer. Further mechanistic speculations concerning the initiation reaction in aliphatic solvents will probably await more data in this area.

In a subsequent section, we shall discuss the effect of polar solvents on the initiation and propagation reactions, but at this point a word about the effect of alkoxides on the initiation step may be in order. Roovers and Bywater⁶⁰ have recently observed that the absence of the induction period in some rate studies in aliphatic solvents may be due to the presence of alkoxide impurities. Figure 16 taken from their paper shows the effect of added *t*-BuOLi on rate of polymerization of isoprene by *sec*-BuLi. It is interesting to note that the presence of lithium *t*-

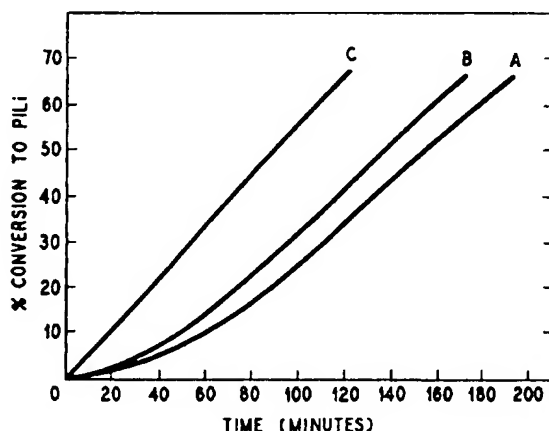


FIG. 16.—Influence of added *t*-BuOLi on the rate of initiation: [isoprene]₀ = 5×10^{-3} M; [*sec*-BuLi]₀ = (A) 1.11×10^{-3} M, (B) 1.46×10^{-3} M, (C) 1.46×10^{-3} M, (D) 1.23×10^{-3} M; [*t*-BuOLi]/[*sec*-BuLi]₀ = (A) 0.0, (B) 0.63, (C) 1.80; *T* = 30° (Ref. 60). Reproduced from *Macromolecules* 1, 328 (1968) with permission of the copyright owner.

butoxide increases the initiation rate while decreasing the propagation rate. Further work in this area⁶¹ indicated that very high concentrations of alkoxides depress the initiation rate, and a generalized explanation is needed. Studies of the effect of alkoxides on the propagation rate are also fragmentary. Brown and coworkers⁸⁴ have deduced that lithium with lithium alkoxide does not fragment (EtLi) data in the presence of alkoxides has been interpreted as aggregates into dimer-alkoxide complexes^{41–43}. It seems unlikely that a mixture of mixed alkoxide-alkyllithium complexes will be the alkyl group, and the alkyl/alkoxide ratio. At high alkoxide concentrations, alkoxide may very well activate the alkyllithium, either by forming a complex or by causing increased dissociation. At low concentrations, complexation may inactivate the lithium alkyl by forming a complex. Further physical evidence is needed to clarify the effect of variation of the alkyllithium on the initiation rate.

The effect of variation of the alkyllithium on the propagation rate has been studied. Workers in the area are aware of the fact that *n*-butyllithium is a more effective initiator than *sec*-butyllithium. Hsieh⁸⁰ has shown that *n*-BuLi is slightly different for dienes, where the *t*-BuLi > *i*-BuLi > *n*-BuLi, than for styrene where *n*-BuLi > *tert*-BuLi, both series having been determined in cyclohexane. Earlier work by Kuntz⁸⁵ with isoprene series: *t*-BuLi > *sec*-BuLi > *i*-PrLi > *n*-BuLi. The behavior of *t*-butyllithium toward the addition reaction is unknown. One is tempted to rationalize the data in terms of electronic factors. However, at the moment there are no speculations.

It should also be noted that the precise mechanism of lithium compound to a mono- or diene has not been established. Workers, including O'Driscoll⁸⁶ and Evans⁷⁹ have discussed mechanisms involving concerted four-center transition state electron transfer steps. At the moment, there is very little evidence which one could deduce the actual mechanism. In view of the complexity of the data in this area, a rationalization in this area is needed.

Finally, we note that several investigations regarding the effect of basic solvents have been made, but we shall reserve a detailed discussion for a later section.

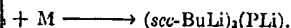
VI. MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Even though the actual mechanism of anionic polymerization of isoprene initiated by alkyllithium may be very complex, the mechanism of cross-association of the organolithium compounds, quite straightforward and is generally believed to be the same as proposed by Ziegler some thirty years ago.



There are no termination and transfer reactions. If the propagation and the growth of all polymer molecules should have a degree of polymerization

of polymer lithium is a sigmoidal function with time in the system *sec*-butyllithium–styrene–cyclohexane. Various data for the systems *n*-BuLi–butadiene–cyclohexane¹⁹, cyclohexane¹⁸, and *sec*-butyllithium–isoprene–*n*-hexane⁶⁰, the slow induction period indicate first-order kinetics for *n*-butyllithium and isoprene⁶¹. Similar kinetic orders were obtained for *sec*-butyllithium–styrene–cyclohexane²¹. Other workers at the period of maximum rate^{18,19,51,82,83}, a region very complicated. The kinetic orders in this region run have been attached to this value. Generally, the induction period is proportional to monomer concentration. Moreover, the induction period is unknown at this time. Bywater and the primary process to be a direct reaction between the tetramer to yield a mixed aggregate species:



ions which might follow this initial step could be of the types (39), (40), and (41). It has been pointed out⁶⁰ that a rate-determining dissociation of the $(\text{sec-BuLi})_4$ to give first-order kinetics in $(\text{sec-BuLi})_4$, but would also lead to mechanistic speculations concerning the initiation which will probably await more data in this area.

We shall discuss the effect of polar solvents on the induction period, but at this point a word about the effect of *t*-BuOLi may be in order. Roovers and Bywater⁶⁰ have shown the effect of the induction period in some rate studies in the presence of alkoxide impurities. Figure 16 shows the effect of added *t*-BuOLi on rate of polymerization. It is interesting to note that the presence of lithium *t*-

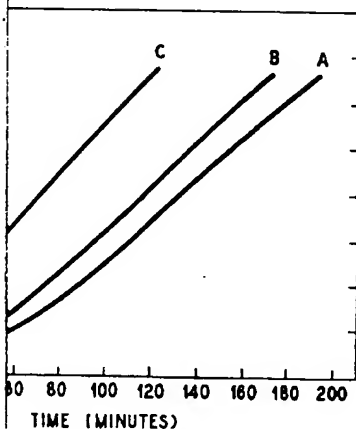


Figure 16. Effect of *t*-BuOLi on the rate of initiation: [isoprene]₀ = 5×10^{-3} M; (A) 1.46×10^{-3} M, (B) 1.46×10^{-2} M, (C) 1.23×10^{-1} M. (B) 0.63, (C) 1.80; $T = 30^\circ$ (Ref. 60). Reproduced with permission of the copyright owner.

butoxide increases the initiation rate while decreasing the propagation rate. However, further work in this area⁶¹ indicated that very high concentrations of butoxide depress the initiation rate, and a generalized explanation for the behavior of alkoxides is needed. Studies of the effect of alkoxides on the structure of alkyllithiums is also fragmentary. Brown and coworkers⁶⁴ have deduced that complexation of ethyllithium with lithium alkoxide does not fragment $(\text{EtLi})_6$. On the other hand, kinetic data in the presence of alkoxides has been interpreted in terms of dissociation of the aggregates into dimer–alkoxide complexes^{41–43}. It seems reasonable that the importance of mixed alkoxide–alkyllithium complexes will be determined by the nature of the alkyl group, and the alkyl/alkoxide ratio. At high values of this ratio, the alkoxide may very well activate the alkyllithium, either by forming more polar aggregates or by causing increased dissociation. At low alkyl/alkoxide ratios, further complexation may inactivate the lithium alkyl by monopolizing all coordination sites. Further physical evidence is needed to clarify our knowledge in this area.

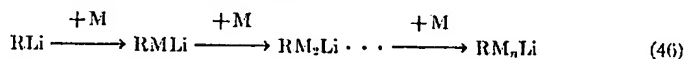
The effect of variation of the alkyllithium on the rates of initiation has received little study. Workers in the area are aware of the fact that *sec*-butyllithium is a more effective initiator than *n*-butyllithium. Hsieh⁶⁵ has shown that the order of reactivity of RLi is slightly different for dienes, where the order is *sec*-BuLi > *i*-PrLi > *t*-BuLi > *i*-BuLi > *n*-BuLi, than for styrene where *sec*-BuLi > *i*-PrLi > *i*-BuLi > *n*-BuLi > *tert*-BuLi, both series having been determined from maximum rate data in cyclohexane. Earlier work by Kuntz⁶⁶ with isoprene yielded a slightly different series: *t*-BuLi > *sec*-BuLi > *i*-PrLi > *n*-BuLi. The reason for the difference in the behavior of *t*-butyllithium toward the addition reactions of diene and styrene is unknown. One is tempted to rationalize the data in terms of an interplay of steric and electronic factors. However, at the moment there are too little data to confirm such speculations.

It should also be noted that the precise mechanism of the addition of an alkyllithium compound to a mono- or diene has not been elucidated at this time. Various workers, including O'Driscoll⁶⁶ and Evans⁷⁹ have discussed possible reaction mechanisms involving concerted four-center transition states as well as consecutive single-electron transfer steps. At the moment, there is very little evidence available from which one could deduce the actual mechanism. In view of the recent flurry of activity relating to radical participation in other alkyllithium reactions^{87–91} more investigation in this area is needed.

Finally, we note that several investigations regarding the initiation reactions in basic solvents have been made, but we shall reserve comment on these data until a later section.

VI. MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

Even though the actual mechanism of anionic polymerization of diene and styrene initiated by alkyllithium may be very complex because of self-association and cross-association of the organolithium compounds, the "nondetailed" scheme is quite straightforward and is generally believed to be the step-wise addition reaction as proposed by Ziegler some thirty years ago.



There are no termination and transfer reactions. If the initiation is not much slower than propagation and the growth of all polymer molecules proceeds simultaneously, the polymer should have a degree of polymerization equal to $(\text{M})_0/(\text{RLi})_0$, where

Theoretical considerations and mathematical tre

concentration and $(\text{RLi})_0$ is the initial initiator concentration. Poisson distribution of molecular weights.

If monomer to *n*-butyllithium or ethyllithium is much higher than the monomer to initiator ratio, not all the initiator reacts. Therefore, under this reaction condition, the actual molecular weight is considerably higher than the theoretical. When a "seeded" initiator was used which isolated initiated polymer from the unreacted initiator, the actual molecular weight was in good agreement between the calculated and experimental values as observed^{51,53}.

The ratio between the calculated kinetic molecular weight M_k , determined viscosity molecular weight M_v , then depends on initiation and propagation. The latter relationship in turn depends on initiator structure. Hsieh⁹⁴ compared the M_k for polyisoprene, polyisoprene, and polystyrene initiated with three different initiators. The results are shown in Table VII.

When *sec*-butyllithium was the initiator, the M_k values for the three monomers were identical within experimental error. This is because *sec*-butyllithium completes the initiation reaction in all cases⁵⁰. The data are also consistent with other kinetic data. At the same *n*-butyllithium concentration the most rapid reaction was found with styrene or isoprene and the least with butadiene. Initiation with *sec*-butyllithium and *tert*-butyllithium no unreacted initiator could be detected at the end of the reaction. With *n*-butyllithium a small amount of unreacted butyllithium was detected at the end of the reaction. Unreacted *n*-butyllithium was found with styrene or isoprene and the least with butadiene. For styrene, *sec*-butyllithium is the fastest; *tert*-butyllithium is the slowest; and for butadiene, *sec*-butyllithium is the fastest; *tert*-butyllithium is the slowest; and for butadiene, *sec*-butyllithium is the fastest; *tert*-butyllithium is the slowest.

In alkyllithium-initiated polymerization, M_k based on kinetic data is approximately equal to the actual molecular weight. The use of M_k to determine the unreacted RLi at the end of polymerization is therefore at initiator level.

TABLE VII
EIGHT M_k VERSUS VISCOSITY-AVERAGE MOLECULAR WEIGHT FOR BUTADIENE, POLYISOPRENE, AND POLYSTYRENE⁹⁴
 $M_v \times 10^{-3}$

Li	<i>sec</i> - and <i>tert</i> -BuLi	Polystyrene		
		<i>n</i> -BuLi	<i>sec</i> -BuLi	<i>tert</i> -BuLi
1	—	490	470	580
2	195	250	196	315
3	97	140	98	190
4	49	75	50	125
5	—	44	26	69
6	19	—	—	—
7	10	21	12	41
8	5	—	—	—

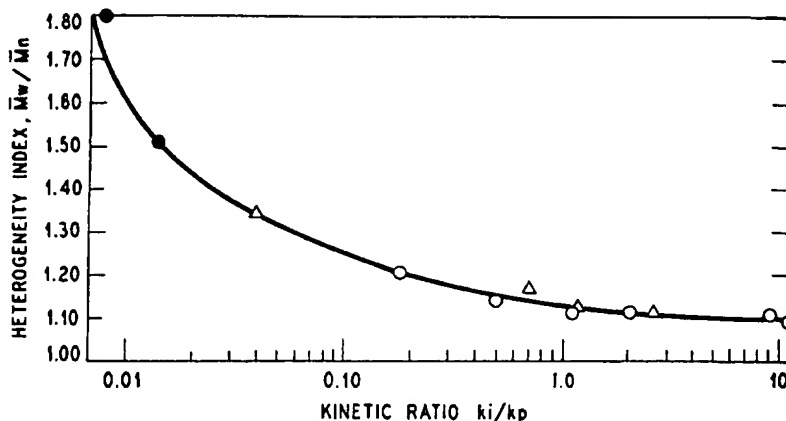


Fig. 17.—Relationship between heterogeneity index as determined by GPC and kinetic ratio⁹⁴. O Polybutadiene, Δ polyisoprene, \bullet polystyrene. Reproduced from *Polymer Letters* 4, 843 (1966) with permission of the copyright owner.

To obtain monodispersed polymer, the following three requirements must be met: (a) all polymer chains must start at the same time; (b) all polymer chains must grow equally; and (c) there must be no termination or transfer. Anionic polymerizations of diene and styrene with alkyllithium initiators closely approach these requirements, and polymers prepared this way generally do have exceptionally narrow molecular weight distribution.

The requirement that all polymer chains start at the same time depends entirely upon the relative rates of initiation and propagation. An excellent correlation between molecular weight distribution and the kinetic ratio was demonstrated by Hsieh and McKinney⁹⁶. The authors prepared polymers of butadiene, isoprene, and styrene in cyclohexane and toluene with *n*-, *sec*-, and *tert*-butyllithiums under otherwise identical conditions. The kinetic ratio, k_i/k_p , was calculated from the published study of rates of initiation and propagation. The heterogeneity index was obtained directly from gel permeation chromatography (GPC). The results are shown in Figure 17.

The values of these heterogeneity indices are a little high since they were obtained from the GPC curves without correction for the peak broadening which occurs in chromatographic columns. For example, the M_w/M_n of 1.80 and 1.12 in Figure 17 were found to be 1.59 and 1.09, respectively, when M_w was determined by light scattering and M_n was determined by the osmotic method.

In the same article it was also shown that small amounts of slowly reacting impurities in the polymerization system have an effect by terminating "living" ends at various states of polymerization. The simultaneous termination, just like simultaneous initiation, causes broadening of the molecular weight distribution. At a constant level of slowly reacting terminators, the effect is negligible at high initiator levels, but becomes increasingly significant as the initiator level is lowered. Figure 18 illustrates this relationship.

By selecting proper reaction conditions and with care, polymers of butadiene, isoprene and styrene with $M_w/M_n \leq 1.10$ have been prepared by alkyllithium initiation^{93,95-97}.

Theoretical considerations and mathematical treatments of "living" polymeriza-

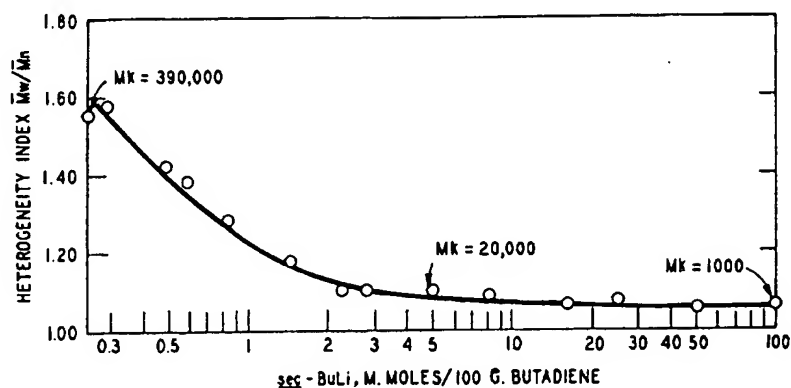


FIG. 18.—Relationship between heterogeneity index from GPC and *sec*-butyllithium level of polybutadiene%. Reproduced from *Polymer Letters* 4, 843 (1966) with permission of the copyright owner.

tion with particular emphasis on molecular weight distribution have been reported in literature. Szwarc and coworkers considered the molecular weight distribution in an ideal "living" system⁹⁸ as well as a nonideal system where a monomer containing small amounts of impurities terminates the growing polymeric molecule⁹⁹. Miyake and Stockmayer¹⁰⁰ obtained complete analytical solutions for the case of constant monomer concentration and analytical approximations for batch polymerizations. Figini¹⁰¹ calculated a theoretical relation between the molecular weight distribution and the stereospecific structure of polymers obtained by anionic, termination-free polymerization. Eisenberg and McQuarrie¹⁰² developed equations for calculating the approximate heterogeneity index to be expected when the polymerization rate constant and the initiation rate are known.

VII. POLYMERIZATIONS OF DIENES AND VINYL MONOMERS IN POLAR SOLVENTS

The over-all polymerization rate in polar solvents, such as ethers and amines, is usually faster than in hydrocarbon solvents. Early work in this area has been reviewed by Bywater⁷³ and by Cubbon and Margerison⁵⁵. Most workers have assumed that the increase in rate is due to increased dissociation of organolithium reagents in basic media. However, the picture is not so simple, as indicated by the effect of small quantities of added tetrahydrofuran on the system polystyryllithium-styrene-benzene as shown in Figure 19¹⁰³. One sees from this work that the effect on the propagation rate is not as large as the effect on the initiation reaction¹⁰⁴, and, furthermore, that the rate of propagation initially increases, passes through a maximum, and falls off to a constant value at high tetrahydrofuran concentrations. The authors attribute this behavior to the formation of four active species, the monomeric organolithium $RMLi$, its dimer, a monoetherate, and a dietherate, all of which compete for monomer in the propagation reaction. The reaction is $\frac{1}{2}$ order with respect to polystyryllithium on the ascending part of the curve, and first order at large excesses of tetrahydrofuran. If one assumes that only dietherates are present in the latter region, then a propagation constant for dietherates of 35 liter/(mole-sec) may be calculated. The maximum rate is apparently due to the participation of more active species, presumably monoetherate. (We shall review later evidence

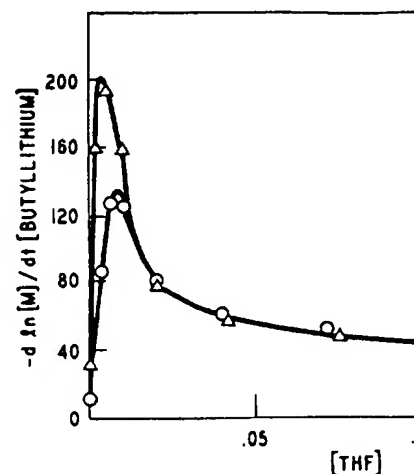
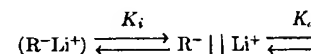


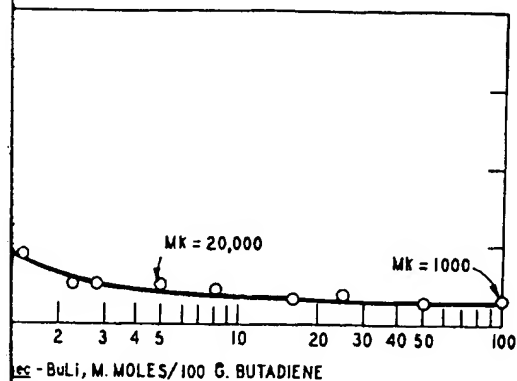
FIG. 19.—The effect of wide variations in the total propagation rate at two median butyllithium concentrations M : Δ , $[BuLi] = 1.2-1.8 \times 10^{-4} M$ (Ref. 103). Reproduced from Research Council of Canada from *Can. J. Chem.* 40, 156

that free ions are present in very small quantities. One may speculate that the higher reactivity of the dietherate, is due to steric effects in the transition state or to the decreased tendency of lithium to coordinate to two oxygen atoms. Morton and coworkers²⁰ have found that the rate of polymerization of isoprene in monoetherates are significant in this system.

Whatever the degree of complexation, the effect apparently to disrupt the dimeric structure of polystyryllithium in hydrocarbon solvents¹⁰⁵. One may imagine several covalent forms, RLi , an intimate or contact ion-pair (with various degrees of "separation"), $R^- Li^+$. Hogen-Esch and Smid³⁷ have shown that fluorescence spectra indicative of equilibria between



In the case of fluorenyllithium in tetrahydrofuran, the ion-pairs $R^- || Li^+$, are indicated from spectral data. The dissociation constant K_i for the dissociation into solvent-separated ion-pairs is <0.01 in dioxane, toluene, and ether, to 4.6 in tetrahydrofuran, dimethylsulfoxide, and dimethoxyethane^{37,106}. The dissociation constant for fluorenyllithium was found to vary from 3.89×10^{-6} to 7.0×10^{-6} at $-70^\circ C$. Thus, the lithium salt consists predominantly of ion-pairs in this solvent with appreciable amounts of free ions. Polystyryllithium has been similarly investigated.



sec-BuLi, M. MOLES/100 G. BUTADIENE

seen heterogeneity index from GPC and sec-butyllithium
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on molecular weight distribution have been reported. Workers considered the molecular weight distribution in well as a nonideal system where a monomer containing terminates the growing polymeric molecule⁹⁹. Miyake complete analytical solutions for the case of constant analytical approximations for batch polymerizations. al relation between the molecular weight distribution re of polymers obtained by anionic, termination-free d McQuarrie¹⁰² developed equations for calculating the index to be expected when the polymerization rate te are known.

IONS OF DIENES AND VINYL MONOMERS IN POLAR SOLVENTS

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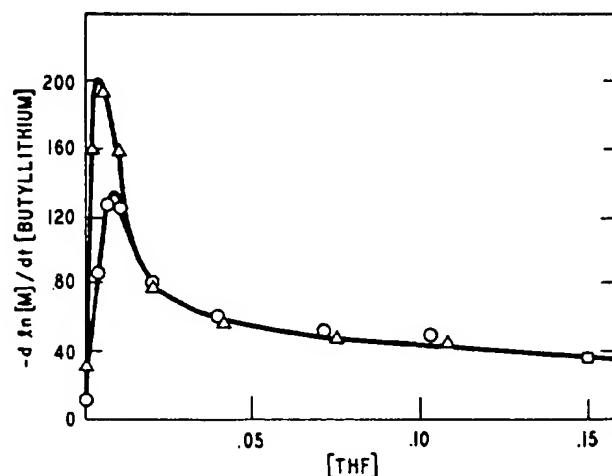
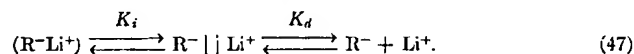


FIG. 19.—The effect of wide variations in the tetrahydrofuran concentration on the propagation rate at two median butyllithium concentrations; O, $[BuLi] = 0.96-1.2 \times 10^{-3} M$; Δ , $[BuLi] = 1.2-1.8 \times 10^{-3} M$ (Ref. 103). Reproduced by permission of the National Research Council of Canada from *Can. J. Chem.* 40, 1504 (1962).

that free ions are present in very small quantities even in excess tetrahydrofuran.) One may speculate that the higher reactivity of the monoetherate, as compared to the dietherate, is due to steric effects in the transition state of the addition process, or to the decreased tendency of lithium to coordinate to an olefin when coordinated to two oxygen atoms. Morton and coworkers³⁰ have studied the effect of tetrahydrofuran on the rate of polymerization of isoprene in hexane, and conclude that only monoetherates are significant in this system.

Whatever the degree of complexation, the effect of strong, neutral Lewis bases is apparently to disrupt the dimeric structure of polystyryllithium which exists in hydrocarbon solvents¹⁰⁵. One may imagine several forms of a monomeric species: a covalent form, RLi , an intimate or contact ion-pair, R^-Li^+ , an agent-separated ion-pair (with various degrees of "separation"), $R^-||Li^+$, and the free ions, R^- and Li^+ . Hogen-Esch and Smid³⁷ have shown that fluorenyllithium compounds show absorption spectra indicative of equilibria between the three ionic forms:



In the case of fluorenyllithium in tetrahydrofuran at $-30^\circ C$, only solvent-separated ion-pairs $R^-||Li^+$, are indicated from spectral data³⁷. The equilibrium constant K_i for the dissociation into solvent-separated ion-pairs at $25^\circ C$ varies from <0.01 in dioxane, toluene, and ether, to 4.6 in tetrahydrofuran, to >50 in pyridine, dimethylsulfoxide, and dimethoxyethane^{37,106}. The amount of free ions in the furan has been obtained from conductance measurements³⁶. The value of K_d for fluorenyllithium was found to vary from $3.89 \times 10^{-6} M$ at $25^\circ C$ to $19.9 \times 10^{-6} M$ at $-70^\circ C$. Thus, the lithium salt consists predominately of solvent-separated ion-pairs in this solvent with appreciable amounts of contact ion-pairs present. Polystyryllithium has been similarly investigated¹⁰. K_d for this compound in tetra-

TABLE VIII
COMPARATIVE KINETIC ORDER FOR ADDITION OF ORGANOLITHIUM REAGENTS TO
1,1-DIPHENYLETHYLENE (DPE) IN THF¹⁰⁹

RLi	Effective reaction order
Methyl	0.27 ± 0.03
Phenyl	0.66 ± 0.04
Vinyl	0.34 ± 0.1
<i>n</i> -Butyl	0.4
Allyl	1
Benzyl	1.1 ± 0.2

hydrofuran at 25° C is $1.86 \times 10^{-7} M$. Unfortunately, a detailed analysis of the absorption spectra of polystyryllithium and polydienyllithium has not been made. The broadness of the absorption bands makes the identification of various discrete species virtually impossible.

The propagation reaction has been studied for polyisoprenyllithium in tetrahydrofuran⁶⁴, ether¹⁰⁸, and in triethylamine^{69,75}. Polybutadienyllithium has been studied in tetrahydrofuran⁶⁴ and in triethylamine^{69,75}. Unfortunately, the absence of complimentary physical data makes these investigations of only limited value at this time. One hopes that conductance and spectroscopic data in these systems will be forthcoming so that the data may be properly analyzed.

Recent kinetic work by Waack and coworkers has illustrated the effect of variation of the organolithium concentration on reaction kinetics. In the reaction with 1,1-diphenylethylene in tetrahydrofuran¹⁰⁹ it was found that the effective reaction order was different for different RLi; the orders being shown in Table VIII.

The 0.66 order with respect to phenyllithium has previously been interpreted in terms of an equilibrium between reactive dimer and monomer¹¹⁰. An important consequence of Waack's work, as shown in Figure 20, is that the relative reactivity of organolithium is dependent upon the concentration range employed. One therefore should be very careful about drawing conclusions from relative reactivity studies until the precise nature of the species and the reaction orders are known. Apparently, the degree of aggregation and/or complexation by tetrahydrofuran of some organolithium is strongly dependent upon the concentration range¹¹¹.

The effective reaction orders shown in Table VIII have been interpreted in terms of the dissociative mechanism, although the nature of the active monomeric species was not discussed. Extrapolation of the data in Figure 20 to dilute solution yields the following relative reactivity order for organolithiums: Group A > Group B > Group C (see Section 1), as would be expected from a consideration of the corresponding carbanions. The reactivity order in the addition reaction to 1,1-diphenylethylene is not the same as for metalation of triphenylmethane¹¹², or for the initiation of styrene polymerization¹¹³, both in tetrahydrofuran. In the latter, the order is sufficiently different from the addition to diphenylethylene—i.e., Group A > Group C > Group B—so as to warrant questions concerning the use of diphenylethylene as a model for the study of vinyl addition reactions. On the other hand, the variation of relative reactivities with concentration¹⁰⁹ makes intercomparisons of this type more dangerous.

VIII. COPOLYMERIZATION

The complete absence of termination and transfer reaction in an alkylolithium initiated polymerization lends itself to the preparation of block copolymers by

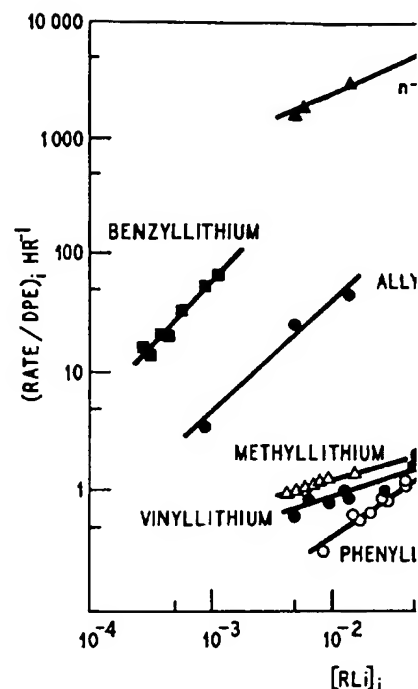


FIG. 20.—Log-log plot of the differential rate expression $(RATE/DPE) / (RLi)$ vs $[RLi]$ to 1,1-diphenylethylene in tetrahydrofuran solution from *J. Am. Chem. Soc.* **91**, 2456 (1969) with permission.

incremental addition of monomers. Block copoly A-B, A-B-A, A-B-A-B-A, etc., may be produced. Some of the polar vinyl monomers such as reactive functional group and other polar monomer sulfides which propagate through $-O-Li^+$ and $-S-$ are polymerized under appropriate conditions as the last i copolymer. A detailed review on the preparation of copolymers was published in 1968¹¹⁴.

Copolymerization initiated with alkylolithium and two hydrocarbon monomers are mixed initially. A polymerization of butadiene-styrene^{69,115-124} and They are particularly interesting because of the phenomenon in hydrocarbon solution which gives the change in copolymerization characteristics in the polar solvent which can give essentially random copolymer.

Let us use the butadiene-styrene example to illustrate. In hydrocarbon solution of an alkylolithium, styrene does not polymerize. However, when a mixture of butadiene and styrene is added, the propagating polymer chains are rich in butadiene. After styrene incorporation suddenly increases ("in the comparison in terms of conversion and time of

TABLE VIII

ORDER FOR ADDITION OF ORGANOLITHIUM REAGENTS TO
DIPHENYLETHYLENE (DPE) IN THF¹⁰⁹

RLi	Effective reaction order
Ethyl	0.27 ± 0.03
Propyl	0.66 ± 0.04
Isopropyl	0.34 ± 0.1
Butyl	0.4
Phenyl	1
Allyl	1.1 ± 0.2

$\times 10^{-7} M$. Unfortunately, a detailed analysis of the
polydiphenyllithium and polydiphenyllithium has not been made.
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COPOLYMERIZATION

termination and transfer reaction in an alkyllithium
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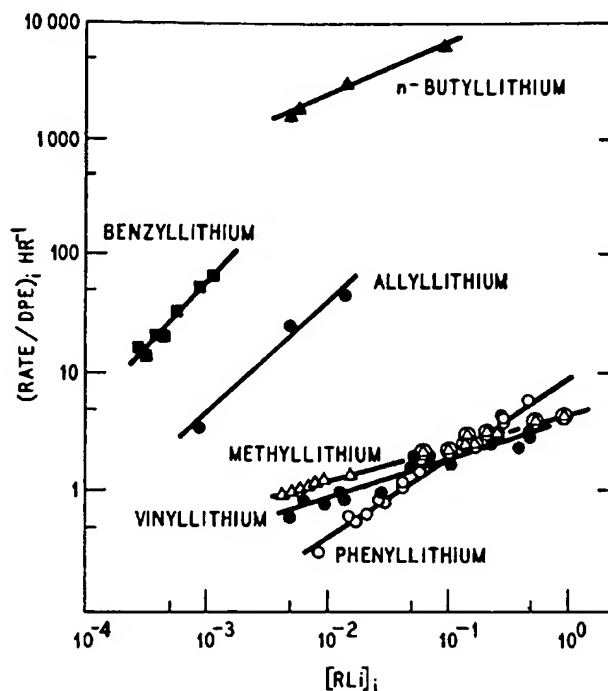


FIG. 20.—Log-log plot of the differential rate expression for addition of the respective RLi to 1,1-diphenylethylene in tetrahydrofuran solution at 22° C (Ref. 109). Reproduced from *J. Am. Chem. Soc.* 91, 2456 (1969) with permission of the copyright owner.

incremental addition of monomers. Block copolymers of different types such as A-B, A-B-A, A-B-A-B-A, etc., may be produced by employing this "living" system. Some of the polar vinyl monomers such as acrylates and nitriles containing reactive functional group and other polar monomers such as formaldehyde and episulfides which propagate through $-O^-Li^+$ and $-S^-Li^+$, respectively, can be polymerized under appropriate conditions as the last increment to prepare the block copolymer. A detailed review on the preparation and properties of these block copolymers was published in 1968¹¹⁴.

Copolymerization initiated with alkyllithium compound also occurs readily when two hydrocarbon monomers are mixed initially. Much work was done on the copolymerizations of butadiene-styrene^{69,115-124} and isoprene-styrene^{69,116,121,122,125-131}. They are particularly interesting because of the observation of the "inversion" phenomenon in hydrocarbon solution which gives essentially block copolymers, and the change in copolymerization characteristics in the presence of small amounts of polar solvent which can give essentially random copolymers.

Let us use the butadiene-styrene example to illustrate the above two points. In hydrocarbon solution of an alkyllithium, styrene polymerizes more rapidly than does butadiene. However, when a mixture of butadiene and styrene is polymerized, the propagating polymer chains are rich in butadiene until late in reaction, whereafter styrene incorporation suddenly increases ("inversion"). Figure 21 illustrates the comparison in terms of conversion and time of reaction. The inflection point in

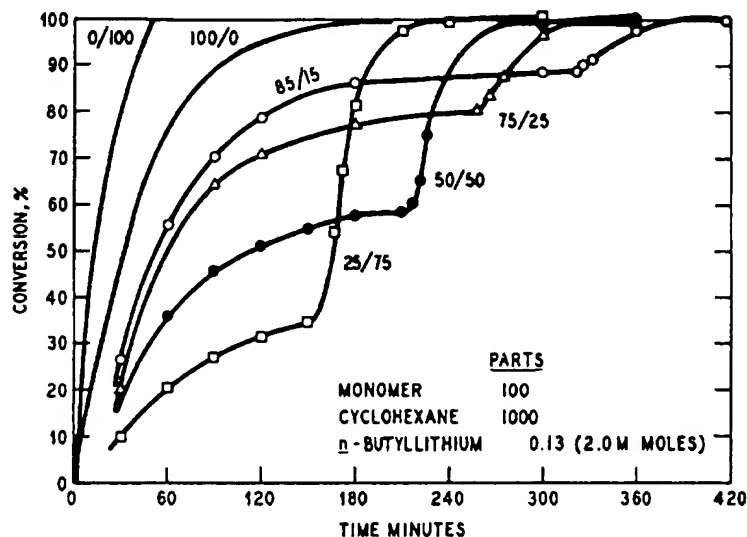


Fig. 21.—Polymerization of butadiene-styrene in cyclohexane at 50° C (Ref. 137).

the conversion curves for the mixtures can be easily identified by the appearance of an orangish-yellow color which is characteristic of polystyryl anion. For the purpose of this discussion, we shall concentrate on the butadiene-to-styrene weight ratio of 75 to 25. As shown in Figure 22, the type of hydrocarbon solvent changes the overall rate, but not the general shape of the curves. As one analyzes polymer samples at various conversions, the results in Figure 23 are obtained. Styrene contents are initially much lower than in the monomer charge, gradually increase until the inflection point of the conversion curve in Figure 23 is attained, and thereafter increase very rapidly. Furthermore, when these samples are analyzed by oxidative degrada-

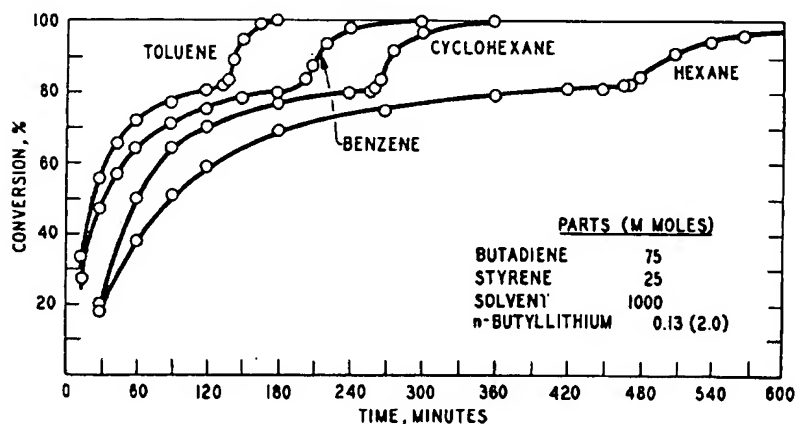


Fig. 22. Polymerization of butadiene-styrene in different solvents at 50° C (Ref. 137).

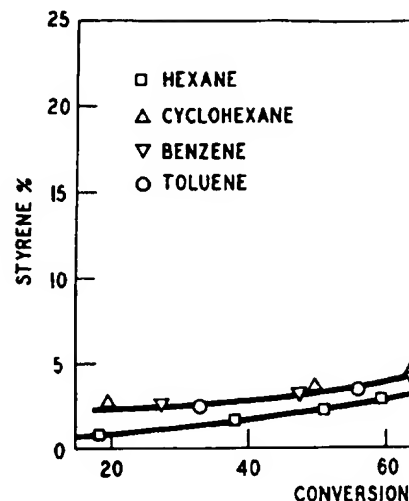


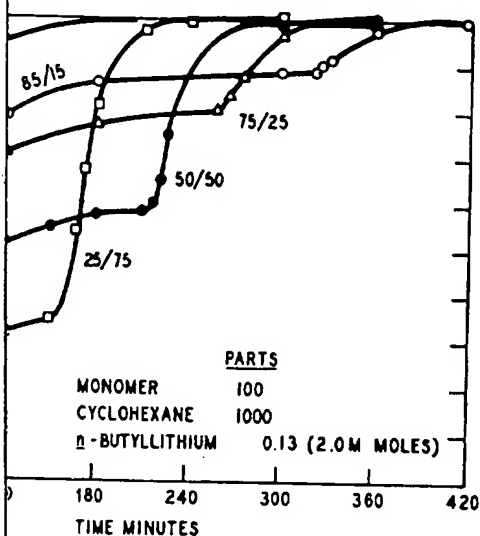
Fig. 23.—Copolymerization of styrene from butadiene

tion¹³², polystyrene segments are recovered or reached, and thereafter increase. Obviously, charged was not polymerized until the diene monomer homopolymerized to form the polystyrene block. It was also reported¹³³ that with

TABLE IX
RELATIVE EFFECTIVENESS OF POLAR COMPOUND
FORMATION IN A 75/25 BUTADIENE STYRENE CHARGE

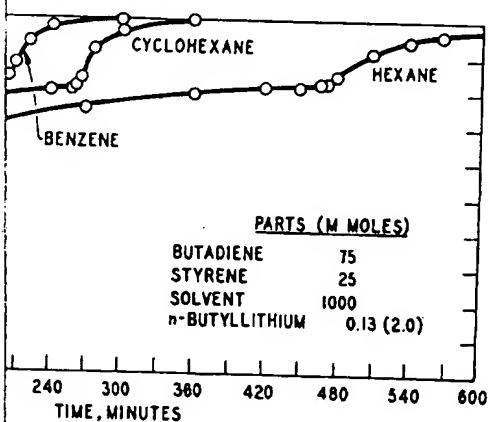
Polar compounds	
Name	g/100 g
Trimethylamine	1
Trimethylamine	1
NNN'-Tetra-	1
Methylethylene diamine	1
NNN'-Tetramethylethylene	1
diamine	1
Dimethoxyethane	1
Dimethoxyethane	1
Butoxyethyl ether	1
Butoxyethyl ether	1
Diethyl ether	1
	10
	15
	20

At 100% conversion as determined by oxidative



butadiene-styrene in cyclohexane at 50° C (Ref. 137).

mixtures can be easily identified by the appearance of a characteristic of polystyryl anion. For the purpose of concentrate on the butadiene-to-styrene weight ratio of 75/25, the type of hydrocarbon solvent changes the overall shape of the curves. As one analyzes polymer samples at 100% conversion, the styrene contents are gradually increased until the inflection point in Figure 23 is attained, and thereafter increase in these samples are analyzed by oxidative degradation.



butadiene-styrene in different solvents at 50° C (Ref. 137).

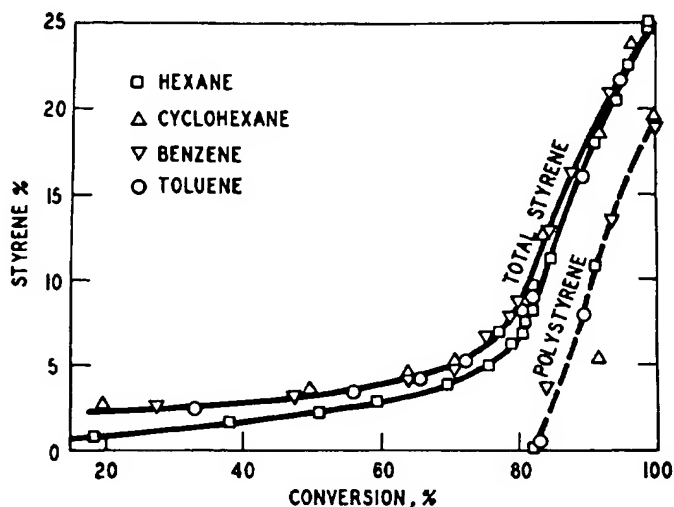


Fig. 23.—Copolymerization of styrene from butadiene-styrene (75/25) at 50° C (Ref. 137).

tion¹³², polystyrene segments are recovered only after the inflection points are reached, and thereafter increase. Obviously, the major portion of the styrene charged was not polymerized until the diene monomer was exhausted, but then it homopolymerized to form the polystyrene block. Isoprene-styrene mixtures gave similar results. It was also reported¹³³ that while isoprene is more reactive than

TABLE IX
RELATIVE EFFECTIVENESS OF POLAR COMPOUNDS IN ELIMINATING POLYSTYRENE
FORMATION IN A 75/25 BUTADIENE STYRENE CHARGE IN CYCLOHEXANE AT 50° C¹³⁷

Polar compounds		Polystyrene, % ^a
Name	g/100 g monomers	
	0	19.0
Trimethylamine	0.5	9.4
Trimethylamine	1.5	6.3
NNN'-Tetra-	0.03	7.2
Methylethylene diamine	0.04	4.4
NNN'-Tetramethylethylene diamine	0.05	0
Dimethoxyethane	0.02	3.6
Dimethoxyethane	0.04	0
Butoxyethyl ether	0.20	0.6
Butoxyethyl ether	0.30	0
Diethyl ether	5.0	4.5
	10.0	2.6
	15.0	0.7
	20.0	0

At 100% conversion as determined by oxidative degradation.

butadiene in homopolymerization, in a mixture butadiene also tends to preferentially polymerized first. Analogous copolymerizations of mixture of isoprene with 1,3-pentadiene¹³⁴, or 2,3-dimethylbutadiene¹³⁴, or 1,3-cyclohexadiene¹³⁵ all show that one member of each pair predominates in polymer at low concentration.

However, addition of small amounts of ethers, tertiary amines, or sulfides^{118,119-120,124-126,126} to the butadiene-styrene or isoprene-styrene copolymerization reduces or eliminates block formation. In some cases, in fact, styrene predominates in polymer at low conversion. The effectiveness of these polar solvents varies significantly as shown in Table IX. The presence of polar compounds also increases the over-all rate of polymerization and changes the stereochemistry of the diene portion of the polymerization.

A novel method to alter copolymerization characteristics is the introduction of Na^+ , K^+ , Rb^+ , or Cs^+ ions in the polymerization system^{138,159}. It was shown⁶¹ that lithium alkoxide reduces the copolymerization rate but does not change the copolymerization characteristics. On the other hand, small amounts of sodium, potassium, rubidium, or cesium *t*-butoxide profoundly affect alkyllithium-initiated copolymerization of butadiene and styrene. When ions of alkali metals other than lithium itself are present, styrene enters the copolymer chain early in the polymerization. For example, at a $\text{RLi}/t\text{-BuOK}$ mole ratio of 1/0.5, the found styrene as a function of conversion curve for a 75/25 butadiene/styrene charge is the same as the curve obtained from phenylpotassium initiation and almost opposite to the curve obtained from butyllithium initiated copolymerization (Figure 24). By adjusting the ratio of butoxide to alkyllithium and selecting proper counter-ion combinations, copolymers of various degree of randomness can be prepared. It was proposed¹³⁹ that there are two counter-ions within the propagating center which can tautomerize to give copolymer chains with microsegments characteristic of each of the counter-ions.

The unusual "inversion" or "reversal" of activities of styrene and the diene in alkyllithium initiated copolymerization in hydrocarbon solvents were attributed to

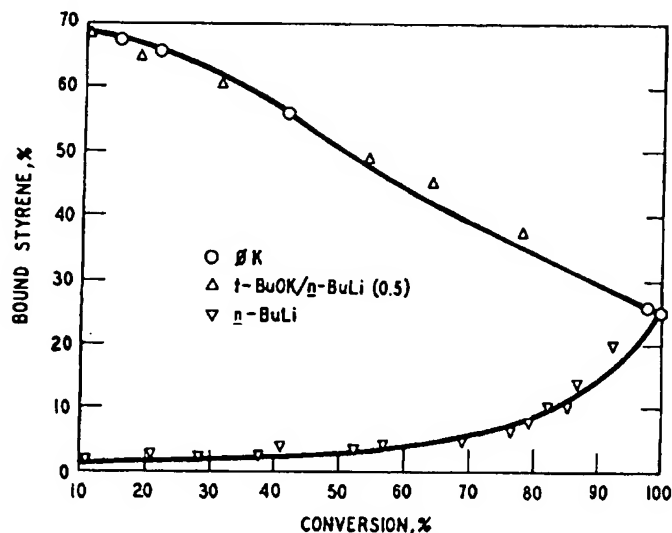


Fig. 24.—Styrene incorporation in butadiene-styrene (75-25) copolymerization in cyclohexane (Ref. 137).

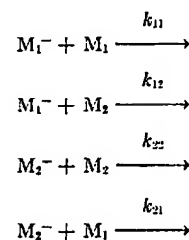
TABLE X
PERCENTAGE STYRENE IN ISOPRENE COPOLYMER A
ISOPRENE 60 TO 40 BY WEIGHT

Solvent	Wt. %	
	1:1	
Benzene	15 ± 1	
Et_3N	59 ± 3	
Et_2O	68 ± 3	
THF	80 ± 6	

a number of different effects. Kelly and Tobolsky in sodium systems in polar and nonpolar solvent composition of the copolymer is related to the carbon-metal bond. Tobolsky and Roger¹³⁶ later attributed the microstructure of the homopolymer to be controlled by the ionic character of the bond with carbon-lithium bond presumably increases as it approaches the ionic character of the carbon-sodium bond.

Franta and Rempp¹⁴⁰ explained the effect of counter-ions. Korotkov¹¹⁵ suggested that the diene in the growing ion-pairs ("living" chain ends) which other words, the growing ion-pairs are preferential which effectively increase the concentration of the diene of the growing ends and hence only this monomer polymerizes. A base such as ether would displace the diene allowing both monomers to polymerize purely as anions.

O'Driscoll and Kuntz¹⁴¹, however, showed that selective solvation mechanism; the seemingly anomalous reaction may be interpreted in terms of classical mechanism developed for free radical polymerization. Thus, the monomer M_1 and M_2 may be written



where M_1^- and M_2^- are propagating polymer chains respectively, assuming the usual steady-state conditions

$$k_{21}(\text{M}_2^-)(\text{M}_1) = k_{12}(\text{M}_1^-)(\text{M}_2)$$

The rates of consumption of monomer M_1 and M_2 are

$$-d(\text{M}_1)/dt = k_{11}(\text{M}_1^-)(\text{M}_1) - k_{21}(\text{M}_2^-)(\text{M}_1)$$

$$-d(\text{M}_2)/dt = k_{12}(\text{M}_1^-)(\text{M}_2) - k_{22}(\text{M}_2^-)(\text{M}_2)$$

in a mixture butadiene also tends to preferentially polymerizations of mixture of isoprene with 1,3-butadiene¹³⁴, or 1,3-cyclohexadiene¹³⁵ all show that minutes in polymer at low concentration.

Small amounts of ethers, tertiary amines, or sulfide-styrene or isoprene-styrene copolymerization. In some cases, in fact, styrene predominates. The effectiveness of these polar solvents varies significantly. The presence of polar compounds also increases ion and changes the stereochemistry of the diene

polymerization characteristics is the introduction of the polymerization system^{138,139}. It was shown⁶¹ that polymerization rate but does not change the copolymer. On the other hand, small amounts of sodium, potassium, profoundly affect alkyllithium-initiated copolymerization. When ions of alkali metals other than lithium itself copolymer chain early in the polymerization. For a ratio of 1/0.5, the found styrene as a function of butadiene/styrene charge is the same as the curve for initiation and almost opposite to the curve obtained for polymerization (Figure 24). By adjusting the ratio selecting proper counter-ion combinations, copolymer can be prepared. It was proposed¹³⁹ that there is a propagating center which can tautomerize to give polymers characteristic of each of the counter-ions. "reversal" of activities of styrene and the diene in polymerization in hydrocarbon solvents were attributed to

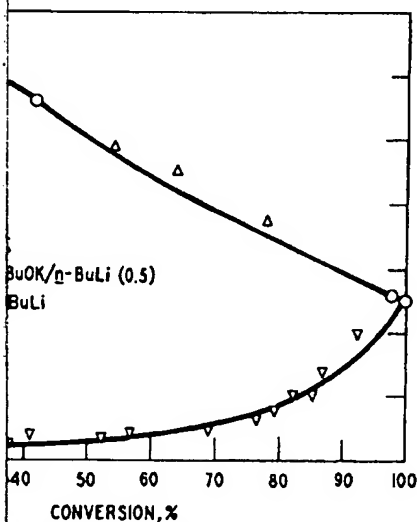


Figure 24. Incorporation in butadiene-styrene (75-25) copolymerization in cyclohexane (Ref. 137).

TABLE X

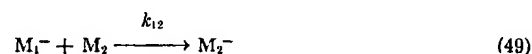
PERCENTAGE STYRENE IN ISOPRENE COPOLYMER AT ZERO CONVERSION—STYRENE TO ISOPRENE 60 TO 40 BY WEIGHT (EQUIMOLAR)¹¹⁶

Solvent	Wt. % of styrene		
	Li	n-BuLi	Na
Benzene	15 ± 1	18 ± 1	66 ± 3
Et ₃ N	59 ± 3	60 ± 3	77 ± 6
Et ₂ O	68 ± 3	68 ± 3	75 ± 6
THF	80 ± 6	80 ± 6	80 ± 6

a number of different effects. Kelly and Tobolsky¹¹⁶, who compared lithium and sodium systems in polar and nonpolar solvents (Table X), proposed that the composition of the copolymer is related to the degree of ionic character of the carbon-metal bond. Tobolsky and Roger¹³⁶ later correlated the copolymer composition with the microstructure of the homopolyisoprene, both of which were reported to be controlled by the ionic character of the growing center. Ether complexing with carbon-lithium bond presumably increases the ionic character and ultimately approaches the ionic character of the carbon-sodium bond.

Franta and Rempp¹⁴⁰ explained the effect on the basis of relative stability of anions. Korotkov¹¹⁶ suggested that the diene monomers are capable of solvating the growing ion-pairs ("living" chain ends) which the styrene is unable to do. In other words, the growing ion-pairs are preferentially solvated (complexed) by diene which effectively increase the concentration of the diene monomers in the vicinity of the growing ends and hence only this monomer is involved in the initial polymerization. A base such as ether would displace the diene in the complex formation allowing both monomers to polymerize purely according to their reactivity.

O'Driscoll and Kuntz¹⁴¹, however, showed that it is not necessary to invoke the selective solvation mechanism; the seemingly anomalous results from copolymerization may be interpreted in terms of classical copolymerization kinetics originally developed for free radical polymerization. Thus, the chain propagation reactions for monomer M₁ and M₂ may be written



where M₁⁻ and M₂⁻ are propagating polymer chains with end units of M₁ and M₂, respectively, assuming the usual steady-state condition

$$k_{21}(M_2^-)(M_1) = k_{12}(M_1^-)(M_2). \quad (52)$$

The rates of consumption of monomer M₁ and M₂ are

$$-d(M_1)/dt = k_{11}(M_1^-)(M_1) + k_{12}(M_2^-)(M_1) \quad (53)$$

$$-d(M_2)/dt = k_{12}(M_1^-)(M_2) + k_{22}(M_2^-)(M_2). \quad (54)$$

From Equations (53) and (54) we obtain

$$\frac{d(M_1)}{d(M_2)} = \left(\frac{M_1}{M_2} \right) \left(\frac{r_1(M_1)/(M_2) + 1}{(M_1)/(M_2) + r_2} \right), \quad (55)$$

where r_1 and r_2 are monomer reactivity ratio defined by

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21} \quad (56)$$

O'Driscoll and Kuntz assumed that both polybutadienyl ion-pair (B^-) and polystyryl ion-pair (S^-) are present in dimeric form and that only the dissociated species are active. Thus, the copolymerization can be described in terms of four reactions and two equilibria.



Where S and B are styrene and butadiene monomers, respectively. Thus

$$[B^-] = [K_B(B^-)_2]^{1/2} \quad \text{and} \quad [S^-] = [K_S(S^-)_2]^{1/2}, \quad (63)$$

and the copolymerization reaction is then described in terms of differential equations

$$-d(B)/dt = k_{BB}^1(B)[(B^-)_2]^{1/2} + K_{SB}^1(B)[(S^-)_2]^{1/2} \quad (64)$$

$$-d(S)/dt = K_{BS}^1(S)[(B^-)_2]^{1/2} + k_{SS}^1(S)[(S^-)_2]^{1/2}. \quad (65)$$

It is assumed that the total concentration of chain ends is constant, the $[(S^-)_2]^{1/2}$ is zero in the initial stages of the reaction, and the steady-state condition exists $K_{BS}(S)[(B^-)_2]^{1/2} = K_{SB}(B)[(S^-)_2]^{1/2}$. After evaluation of all the parameters, it is then possible to calculate the monomer concentrations (B) and (S) as a function of time by numerically integrating Equations (64) and (65). The authors have done this, hour by hour, and showed the very good agreement between the experimental data¹²⁰ and the calculated lines (Figure 25).

The determination of reactivity ratios based on the usual relation between copolymer composition and monomer ratio, however, can only be considered as an approximation. Anionic copolymerization involves no steady state of propagating chains even if the initiation is instantaneous. In many cases, initiation by the alkyl-lithium continues during polymerization and may even affect the reactivity ratio as shown in styrene-methylmethacrylate case¹⁴². Preferential initiation of styrene in the presence of butadiene, for example, has been observed¹⁴³.

Morton and Ellis¹²³ obtained the reactivity ratios of the butadiene-styrene system in benzene by direct measurement of the absolute rates. The values of homopropagation

ALKYL LITHIUM POLYM

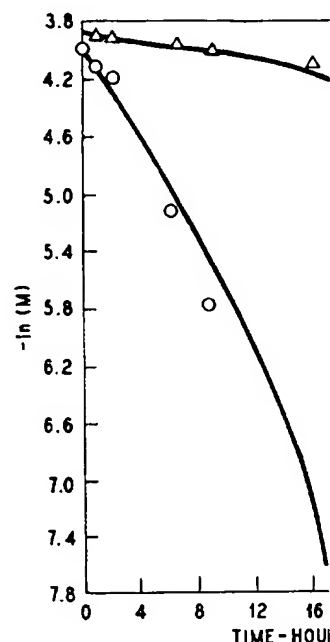


Fig. 25.—Copolymerization rates at 30° C in benzene: (O) butadiene, experimental; (—) calculated. *J. Polymer Sci.* **61**, 19 (1962) with permission of the copyright owner.

rate constants, K_{BB} and K_{SS} , are already known, and so only the two cross-propagation rates, K_{BS} and K_{SB} , need to be determined. Fortunately, the optical spectrum of S^- anion differs from that of B^- , and the optical spectrum of S^- anion differs from that of B^- . The authors have determined the optical spectrum of S^- anion and had to be estimated. Their results show $K_{BB} > K_{BS}$, which explains the anomalous behavior of the butadiene-styrene system and confirms the results of Kuntz¹⁴¹.

Johnson and Worsfold¹⁴⁷ determined absolute rates for the styrene system in cyclohexane. They also found that polystyryl anion is virtually instantaneous. Their earlier observation that homopolymerization of butadiene monomer still remains in solution. Worsfold's results in the styrene system in cyclohexane. It was shown that the results adequately explain the peculiar behavior of the styrene system.

The rate of styrene addition to either polystyryl anion was shown by a photometric technique^{147,148} of these diene monomers. These results, therefore, explain the solvation of growing chain ends by the diene.

Although kinetics explain the "inversion" of the diene-styrene quite successfully, it is nevertheless

we obtain

$$\left(\frac{M_1}{M_2}\right) \left(\frac{r_1(M_1)/(M_2) + 1}{(M_1)/(M_2) + r_2} \right), \quad (55)$$

activity ratio defined by

$$r_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21} \quad (56)$$

that both polybutadienyl ion-pair (B^-) and polystyrene in dimeric form and that only the dissociated species can be described in terms of four reactions



butadiene monomers, respectively. Thus

$$[B^-]^{1/2} \text{ and } [S^-] = [K_S(S^-)_2]^{1/2}, \quad (63)$$

is then described in terms of differential equations

$$[B] \frac{d[B^-]^{1/2}}{dt} + K_{st} [B] [S^-]^{1/2} \quad (64)$$

$$[S] \frac{d[S^-]^{1/2}}{dt} + k_{ss} [S] [S^-]^{1/2} \quad (65)$$

Concentration of chain ends is constant, the $[S^-]^{1/2}$ reaction, and the steady-state condition exists $[B^-]^{1/2}$. After evaluation of all the parameters, it is possible to plot monomer concentrations (B) and (S) as a function of time. Equations (64) and (65). The authors have done a very good agreement between the experimental data (Figure 25).

Activity ratios based on the usual relation between monomer ratio, however, can only be considered as an approximation. In many cases, initiation by the alkylization is not instantaneous. In many cases, initiation by the alkylization and may even affect the reactivity ratio. In the styrene case¹⁴². Preferential initiation of styrene monomer, has been observed¹⁴³.

The reactivity ratios of the butadiene-styrene system are not known. The values of homopropagation

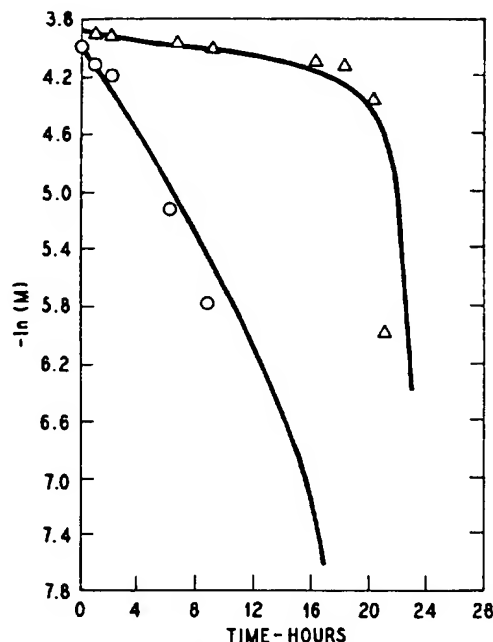


Fig. 25.—Copolymerization rates at 30° C in heptane, 0.017M: (Δ) styrene, experimental; (O) butadiene, experimental; (—) calculated curves (Ref. 141). Reproduced from *J. Polymer Sci.* 61, 19 (1962) with permission of the copyright owner.

rate constants, K_{BB} and K_{SS} , are already known from their previous work¹⁴¹ and so only the two cross-propagation rates, K_{BS} and K_{SB} , were unknown. Fortunately, the optical spectrum of S^- anion differs from that of B^- , so the reactions of $B^- + S \rightarrow S^-$ and $S^- + B \rightarrow B^-$ can be followed spectrophotometrically. The reaction between butadiene monomer and polystyryl anion is too rapid to determine accurately and had to be estimated. Their results clearly showed that $K_{SB} \gg K_{SS} > K_{BB} > K_{BS}$, which explains the anomalous copolymerization behavior of the butadiene-styrene system and confirms the scheme proposed by O'Driscoll and Kuntz¹⁴¹.

Johnson and Worsfold¹⁴⁷ determined absolute rate constants for the butadiene-styrene system in cyclohexane. They also found that the addition of butadiene to polystyryl anion is virtually instantaneous. This is in perfect agreement with the earlier observation that homopolymerization of styrene does not occur so long as butadiene monomer still remains in solution. Worsfold¹⁴⁸ also studied the isoprene-styrene system in cyclohexane. It was shown that $K_{SI} > K_{SS} > K_{II} > K_{IS}$, which adequately explains the peculiar behavior of the styrene-isoprene system.

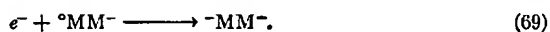
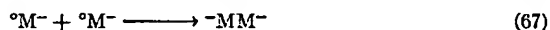
The rate of styrene addition to either polybutadienyl anion or polyisoprenyl anion was shown by a photometric technique^{147,148} not to be lowered in the presence of these diene monomers. These results, therefore, directly challenge the hypothesis of solvation of growing chain ends by the diene.

Although kinetics explain the "inversion" behavior in copolymerizations of diene-styrene quite successfully, it is nevertheless only a formal account of what

happens. It does not provide a mechanism which is responsible for this behavior. The selective solvation mechanism, as was pointed out earlier, is theoretically sound and is not disproved. Preferential solvation was invoked by Overberger and his associates¹⁴⁴ in their study of anionic copolymerization of styrene and substituted styrenes. They concluded that determination of reactivity ratios as defined for radical systems¹⁴⁵⁻¹⁴⁷ did not fully characterize homogeneous anionic copolymerizations. It is obvious that the final elucidation of the actual copolymerization mechanism will have to await definitive mechanisms on homopropagations and the interactions between organolithium compounds and unsaturated monomers and polar materials.

Evans and George¹⁴⁸ have reported that butyllithium adds faster to 1,1-diphenylethylene than to styrene, but the former olefin cannot dimerize, probably because of the steric hindrance due to the second phenyl group in the 1,1-diphenylethylene. Yuki and his colleague¹⁴⁹⁻¹⁵¹ studied the copolymerizations of 1,1-diphenylethylene (M_2) as well as *trans*-stilbene (M_2) with styrene (M_1) and a conjugated diene (M_1). The rate constant K_{22} must be zero, and, if the rate constant K_{11} is sufficiently smaller than K_{12} , it is also expected that the crossover propagation must occur predominantly and result an alternating copolymerization of M_1 and M_2 . In fact, in tetrahydrofuran, both 1,1-diphenylethylene and *trans*-stilbene gave alternating copolymers with butadiene, isoprene, and 2,3-dimethylbutadiene. In benzene, however, 1,1-diphenylethylene is copolymerized alternatively by *n*-butyllithium only with 2,3-dimethylbutadiene and gave diene-rich copolymers with butadiene and isoprene. *trans*-Stilbene copolymerized with 2,3-dimethylbutadiene, but gave a diene-rich copolymer in benzene. Attempts to copolymerize stilbene or isoprene produced only diene homopolymers. For 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in tetrahydrofuran, the authors reported $K_{11} = 1.4 \times 10^{-3}$ liter/mole-sec and $K_{21} = 1.3$ to 1.8×10^{-3} liter/mole-sec at 22°C. On the other hand, styrene seemed to be incorporated into copolymers more easily in hydrocarbon solvent than in tetrahydrofuran, and gave styrene-rich copolymers both with 1,1-diphenylethylene and with *trans*-stilbene. The monomer reactivity ratio r , was obtained from the copolymer composition at the complete consumption of M_1 , assuming the rate constant $K_{22} = 0$. The reactivity ratio was affected by the solvent but not by the catalyst (butyllithium, sodium-naphthalene, or potassium dispersion) or reaction temperature. Alternating copolymer of ethylene and 2-methylstyrene can also be prepared with *n*-butyllithium in tetrahydrofuran at low and high pressures¹⁵².

Copolymerization of styrene and methyl methacrylate by lithium metal has been examined by a number of investigators¹⁵³⁻¹⁶⁰. Use of the metallic lithium as initiator leads to a heterogeneous catalysis as contrasting to the homogeneous alkyllithium reaction. Tobolsky¹⁵⁴ and Overberger¹⁶¹ extended Szwarc's electron transfer mechanism for sodium-naphthalene initiation in ether to lithium metal catalysis.



The radical ends produced by electron transfer initiation are short-lived and couple to give the dianion. The latter propagates in a typical homogeneous anionic

style with the exception that now it is growing a that the copolymerization of isoprene and styrene with metallic lithium dispersion are virtually identical.

However, on the copolymerization of methyl methacrylate and styrene, Boudreau and Tobolsky¹⁵⁴⁻¹⁵⁵ found that the copolymerization in a variety of different solvents gave low conversion and copolymers produced with incorporated only a trace (<1%) of styrene. On the other hand, the copolymerization gives a 50-50% copolymer¹⁶², able to grow simultaneously by a radical anion. Tobolsky and Hartley¹⁶³ suggested that in the copolymerization, the transfer from radical-ion to anionic propagation is negligibly small. In the acrylate and styrene with metallic lithium, the initiator and the relative amount of free radical propagation is considerable. The authors develop the mechanism of ionic propagation as a function of conversion.

Pluymers and Smets¹⁶⁰ showed that increasing the styrene content of the copolymer feed increased the styrene content of the copolymer. The reaction mixture reduced the relative styrene content of the copolymer. These authors supported the radical-anionic mechanism of O'Driscoll.

Mulvaney, Overberger and Scheller¹⁵⁶ point out that Tobolsky and coworkers could also be interpreted to suggest that since the polymerization was initiated by metallic lithium, styrene molecules could be initiated during the ensuing anionic propagation. George and Tobolsky¹⁶⁴ that the number of styrene molecules initiated by the mechanism that is initiation reaction. Subsequently, Overberger¹⁶⁵ there was no random sequence of styrene and styrene in the copolymers prepared with metallic lithium as initiator. They found that the copolymerization is stopped at low conversion content which sometimes exceeds the value expected. This led them to postulate that styrene molecules are positively charged lithium metal and that the chain ends on the surface cause preferential polymerization.

The published data on reactivity ratios and copolymer compositions as well as from rate measurements

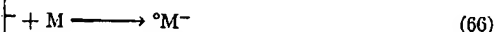
IX. POLYMERIZATION OF POLYMERIZATION

In addition to conjugated dienes and vinyl monomers can be polymerized with alkyllithium carried out at low temperature to minimize side reactions. Lithium initiated polymerizations of acrylates¹⁷²⁻¹⁷⁵, dimethylketene¹⁷⁶, isocyanates¹⁷⁷, a

mechanism which is responsible for this behavior. As was pointed out earlier, is theoretically sound. Solvation was invoked by Overberger and his anionic copolymerization of styrene and substituted determination of reactivity ratios as defined for allyl characterize homogeneous anionic copolymerization. Elucidation of the actual copolymerization mechanism on homopropagations and the intercompounds and unsaturated monomers and polar

ported that butyllithium adds faster to 1,1-diphenylethylene than to 1,2-diphenylethylene. The former olefin cannot dimerize, probably because of the second phenyl group in the 1,1-diphenylethylene. Studied the copolymerizations of 1,1-diphenylethylene (M_2) with styrene (M_1) and a conjugated diene (M_1). K_{11} is zero, and, if the rate constant K_{11} is sufficiently small, it is expected that the crossover propagation must occur in alternating copolymerization of M_1 and M_2 . In fact, 1,1-diphenylethylene and *trans*-stilbene gave alternating copolymers, and 2,3-dimethylbutadiene. In benzene, 1,1-diphenylethylene is copolymerized alternatively by *n*-butyllithium and gave diene-rich copolymers with butadiene copolymerized with 2,3-dimethylbutadiene, but gave no copolymer. Attempts to copolymerize stilbene or isoprene with 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in tetrahydrofuran, the authors reported $K_{11} = 1.4 \times 10^{-3}$ and 1.8×10^{-3} liter/mole-sec at 22°C. On the other hand, 1,1-diphenylethylene copolymerized more easily in hydrocarbon solvents, and gave styrene-rich copolymers both with 1,1-diphenylethylene and *trans*-stilbene. The monomer reactivity ratio r , was determined at the complete consumption of M_1 , $r = 0$. The reactivity ratio was affected by the solvent used: lithium, sodium-naphthalene, or potassium diphenylacetylene. Alternating copolymer of ethylene and 2-methyl-2-butene with *n*-butyllithium in tetrahydrofuran at low and

and methyl methacrylate by lithium metal has been reported by investigators¹⁵³⁻¹⁶⁰. Use of the metallic lithium as a catalyst as contrasting to the homogeneous system¹⁵⁴ and Overberger¹⁶¹ extended Szwarc's electron transfer initiation in ether to lithium metal



by electron transfer initiation are short-lived and after propagates in a typical homogeneous anionic

style with the exception that now it is growing at both ends. Indeed, it was shown¹¹⁶ that the copolymerization of isoprene and styrene with butyllithium and with metallic lithium dispersion are virtually identical.

However, on the copolymerization of methyl methacrylate and styrene, O'Driscoll, Boudreau and Tobolsky¹⁵⁴⁻¹⁵⁸ found that copolymers produced with a lithium dispersion in a variety of different solvents contained considerable styrene at low conversion and copolymers produced with purely anionic initiator (BuLi) incorporated only a trace (<1%) of styrene. On the basis of the fact that purely radical copolymerization gives a 50-50% copolymer¹⁶⁷, they postulated a polymeric species able to grow simultaneously by a radical and an anionic mechanism¹⁵⁴. Later Tobolsky and Hartley¹⁶⁸ suggested that in the one case, such as isoprene-styrene copolymerization, the transfer from radical-ion to monomer is instantaneous and virtually complete. The relative amount of free radical propagation as compared to anionic propagation is negligibly small. In the copolymerization of methylmethacrylate and styrene with metallic lithium, there is a continuous feed of radical-ion initiator and the relative amount of free radical propagation as compared to anionic propagation is considerable. The authors developed exact expressions for radical versus ionic propagation as a function of conversion.

Plumbers and Smets¹⁶⁰ showed that increasing the mole fraction of styrene in the feed increased the styrene content of the copolymers, and that adding benzoquinone to the reaction mixture reduced the relative importance of anionic growth and increased the styrene content of the copolymers appreciably. Based on these data, these authors supported the radical-anionic mechanism proposed by Tobolsky and O'Driscoll.

Mulvaney, Overberger and Scheller¹⁵⁶ pointed out that the results obtained by Tobolsky and coworkers could also be interpreted by another mechanism. It was suggested that since the polymerization was heterogeneous with respect to the initiator, styrene molecules could be initiated on a statistical basis and be polymerized during the ensuing anionic propagation. However, it was pointed out by George and Tobolsky¹⁶⁴ that the number of styrene units per chain was too large to be totally explained by the mechanism that styrene is incorporated only in the initiation reaction. Subsequently, Overberger and Yamamoto^{157,158} reported that there was no random sequence of styrene and methyl methacrylate units in these copolymers prepared with metallic lithium and, therefore, there was no radical propagation in this copolymerization. They found that block copolymers are produced which consist of a polystyrene part and polymethyl methacrylate part. When the copolymerization is stopped at low conversion, the copolymer has a high styrene content which sometimes exceeds the value expected for radical copolymerization. This led them to postulate that styrene molecules are absorbed on the surface of the positively charged lithium metal and that the free ion character of the growing chain ends on the surface cause preferential polymerization of styrene in the early stage.

The published data on reactivity ratios determined from initial copolymer compositions as well as from rate measurements are recorded in Table XI.

IX. POLYMERIZATION OF POLAR MONOMERS

In addition to conjugated dienes and vinyl aromatic monomers, several polar monomers can be polymerized with alkyllithium initiators in reactions generally carried out at low temperature to minimize side reactions. For examples, alkyllithium initiated polymerizations of acrylates¹⁶⁷⁻¹⁶⁹, acrylamides^{170,171}, vinyl ketones¹⁷²⁻¹⁷⁶, dimethylketene¹⁷⁶, isocyanates¹⁷⁷, aldehydes¹⁷⁷⁻¹⁸¹, vinyl chloride¹⁸²⁻¹⁸³,

TABLE XI
REACTIVITY RATIOS IN LITHIUM INITIATED COPOLYMERIZATION

M ₁	M ₂	Solvent	Temp., °C	r ₁	r ₂	Ref.
Styrene	Butadiene	Toluene	25	0.1	12.5	122
		Benzene	30-50	0.05	15	115
		Heptane	30	0	7	120
		Benzene	29	0.06	3 ^a	123
		Cyclohexane	40	<0.04	26 ^a	117
		Ether	30	0.11	1.78	119
		THF	-35	0.8	0.2	122
		THF	30	0.77	1.03	124
		Toluene-TEA (60-40)	25	0.3	5.5	124
Styrene	Isoprene	Toluene	27	0.25	9.5	122
		Benzene	30	0.14	7	125
		Cyclohexane	40	0.046	16.6 ^a	128
		THF	27	9	0.1	122
		THF	-35	40	0	122
		TEA	27	0.8	1.0	122
Isoprene	Butadiene	Hexane	50	0.47	3.4	133
Isoprene	1,3-Pentadiene	Hexane	50	17	0.06	134
Styrene	Vinyltrimethylsilane	Heptane	12	5.7	0.06	165
Styrene	1,1-Diphenylethylene	THF	30	0.13	— ^b	149, 150
		Toluene	30	0.04	— ^b	149, 150
		Benzene	30	0.71	— ^b	149, 150
		Hexane	30	0.63	— ^b	149, 150
Styrene	<i>p</i> -Methoxystyrene	THF	0	2.9	0.23 ^c	145
		Toluene	0	10.9	0.05	145
		THF	0	1.3	0.9 ^c	145
<i>p</i> -Methylstyrene	<i>p</i> -Methoxystyrene	Toluene	0	2.5	0.26	145
		THF	0	1.93	0.72 ^c	145
Methylmethacrylate	Acrylonitrile	Bulk	-8	0.39	7	166
Styrene	Acrylonitrile	Iso-octane or ether	-12	0.20	14	166

^a From rate measurements.

^b $k_{22} = 0$.

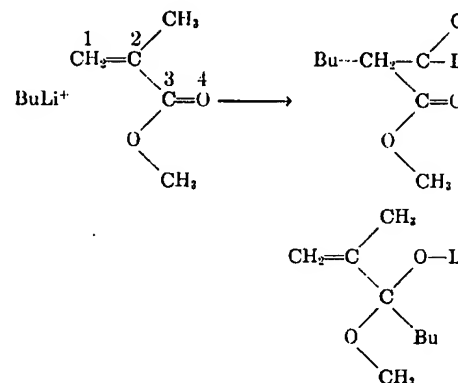
^c Li metal initiation; all other RLi initiation.

vinilidene chloride¹⁸⁴ and others have been reported. Alternating copolymers of dimethylketene and aliphatic and aromatic aldehydes were prepared with alkyl-lithium initiation¹⁸⁵.

Only in the case of methyl methacrylate is detailed kinetic information available. To a lesser extent, acrylonitrile has also been examined. For this review, we shall confine our discussion to these two monomers.

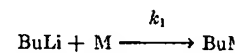
ALKYL LITHIUM POLYMER

Korotkov and coworkers¹⁸⁶ examined the polymerization of methyl methacrylate with *n*-butyllithium in toluene solution. They observed that only a small part of the *n*-butyllithium produce active centers. In addition, the molecular weight increases with the degree of conversion; and after reacted, an approximate doubling of molecular weight that *n*-butyllithium can react with methyl methacrylate at the 1,2-addition positions and suggested that only the 1,2-addition polymerization.

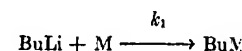


The above modes of addition may be extended to other monomers, but they can also "perish" if these molecules react with the monomer or with the polymer. The following mechanism is suggested by Korotkov and coworkers to describe the polymerization of methyl methacrylate in toluene.

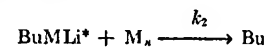
1. Creation of the active polymerization centers:



2. Creation of the inactive products by the attack of the monomer:



3. Propagation of polymer chains:



4. Termination of polymer chains by the attacking of the monomer or polymer:

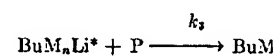
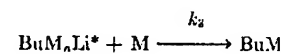


TABLE XI
N LITHIUM INITIATED COPOLYMERIZATION

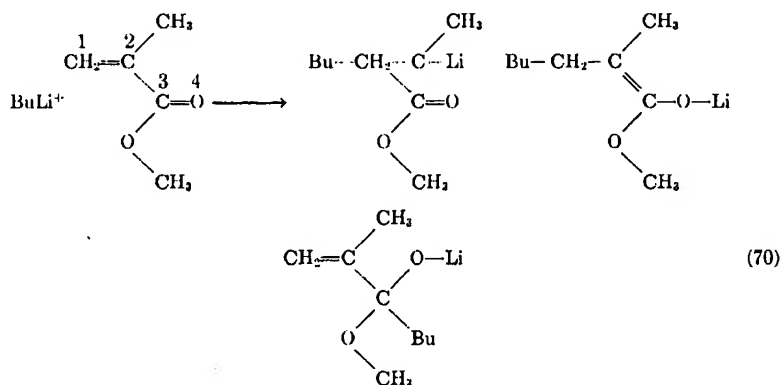
Solvent	Temp., ° C	r ₁	r ₂	Ref.
Toluene	25	0.1	12.5	122
Benzene	30-50	0.05	15	115
Hexane	30	0	7	120
Benzene	29	0.06	3 ^a	123
Cyclohexane	40	<0.04	26 ^a	117
Hexane	30	0.11	1.78	119
HF	-35	0.8	0.2	122
HF	30	0.77	1.03	124
Toluene-TEA (60-40)	25	0.3	5.5	124
Toluene	27	0.25	9.5	122
Benzene	30	0.14	7	125
Cyclohexane	40	0.046	16.6 ^a	128
HF	27	9	0.1	122
HF	-35	40	0	122
EA	27	0.8	1.0	122
Hexane	50	0.47	3.4	133
Hexane	50	17	0.06	134
Hexane	12	5.7	0.06	165
HF	30	0.13	— ^b	149, 150
Toluene	30	0.04	— ^b	149, 150
Benzene	30	0.71	— ^b	149, 150
Hexane	30	0.63	— ^b	149, 150
HF	0	2.9	0.23 ^a	145
Toluene	0	10.9	0.05	145
HF	0	1.3	0.9 ^c	145
Toluene	0	2.5	0.26	145
HF	0	1.93	0.72 ^c	145
EA	-8	0.39	7	166
Octane or ether	-12	0.20	14	166

initiation.

have been reported. Alternating copolymers of aromatic aldehydes were prepared with alkyl-

acrylate is detailed kinetic information available, has also been examined. For this review, we shall use monomers.

Korotkov and coworkers¹⁶⁶ examined the polymerization of methyl methacrylate with *n*-butyllithium in toluene solution in the range from -50 to -80° C. They observed that only a small part of the *n*-butyllithium introduced reacts to produce active centers. In addition, the molecular weight of polymer obtained increases with the degree of conversion; and after about 80% of the monomer has reacted, an approximate doubling of molecular weight takes place. They pointed out that *n*-butyllithium can react with methyl methacrylate in the 1,2-, 1,4-, or 3,4-positions and suggested that only the 1,2-addition product is active in the polymerization.

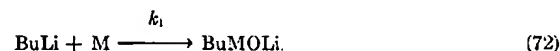


The above modes of addition may be extended to the active polymer centers which can also "perish" if these molecules react with the monomer in 1,4- or 3,4-positions or with the polymer. The following mechanism was proposed by Korotkov and coworkers to describe the polymerization of methyl methacrylate by butyllithium in toluene.

1. Creation of the active polymerization centers:



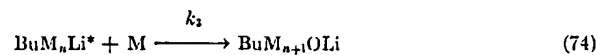
2. Creation of the inactive products by the attack of butyllithium at the ester group of the monomer:



3. Propagation of polymer chains:



4. Termination of polymer chains by the attacking of active centers at ester group of the monomer or polymer:

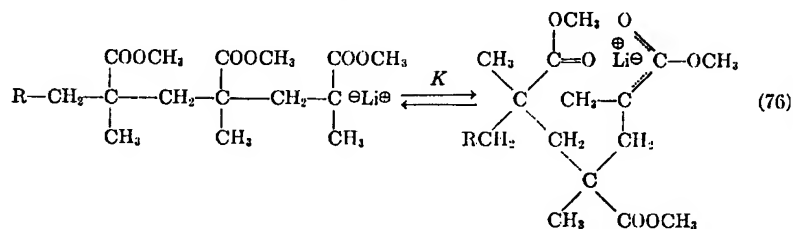


To develop kinetic equations based on the proposed reaction scheme requires drastic simplification. The final derived equations are valid only at very low conversions where termination reactions are not important.

Glusker^{187,188} studied the polymerization of methyl methacrylate in toluene-ether solutions at temperatures in the range of -50° to -78° C with 9-fluorenyllithium as the initiator. The strong ultraviolet absorption of the fluorenyl group was utilized to determine amounts of initiator fragments bound to the polymer chain. The termination with tritium-labelled acetic acid allows one to calculate the concentration of active chain ends. Comparison of these two independent measurements gives the percentage of chains which were active when the terminator was added. Based on these data, it was concluded that one fluorenyl group becomes chemically attached to each polymer chain and essentially all of the initiator reacts with the monomer within 5 seconds after mixing, and termination reactions are very slow or nonexistent. At -78° C, between 75% and 100% of the polymer chains were found to be active at the end of polymerization.

The fast initiation, slow propagation, and the lack of termination should produce a monodispersed polymer. Contrary to this prediction, fractionation¹⁸⁸ indicated that: (1) the molecular weight distribution of these polymers is bimodal; (2) more than 90 mole % of the polymer chains has a molecular weight less than 2000; (3) these low molecular weight chains add tritium upon reaction with tritium-labelled acetic acid and do not, therefore, result from permanent termination reactions; (4) the molecular weight distribution of the high polymer fraction from countercurrent extraction is sufficiently broad to approximate log-normal distribution; and (5) increasing the ether in toluene causes decreases in isotacticity and narrower molecular weight distribution. Kinetics were measured in 90% toluene/10% diethyl ether (by volume) at -60° C. These experiments showed that: (1) the rate of polymerization appears to be first order in monomer and remains constant to very high conversion; (2) plots of $-\ln M/M_0$ as a function of time (where M and M_0 represent monomer concentrations at time t and 0, respectively) can be extrapolated to a finite conversion intercept at zero time; (3) this conversion corresponds to that required to form a species containing one fluorenyl group and three monomer units; and (4) plots of number-average molecular weight as a function of time converge to the same intercept at zero time, regardless of the ratio of initial concentration of monomer to that of initiator, and that intercept is the molecular weight of the species just mentioned (one fluorenyl group and three monomer units).

The authors proposed a mechanism which is based on all these data as follows: After very rapid initiation, monomer addition proceeds until three monomer units are added to each molecule. A high percentage of the total number of chains started to undergo "pseudo termination" by forming the cyclic complex to which further monomer may add only with difficulty.



There is a very pronounced reduction in the probability of cyclization when the

chain length reaches eight or nine monomer units. high molecular weights. It is necessary to postulate centers is achieved to account for the first-order kinetics to high conversion. The authors originally suggested that termination is a function of the configurations of the last three monomer units and that the decrease in probability of cyclization of ten monomer units is due to the formation of the helical favors isotactic propagation. However, their later work on termination of the low molecular weight polymers of atactic and isotactic propagations. The hypothesis that the constants for cyclization are the predominant result of the last three units at the end of polymer chain and how initial conditions affect the equilibrium constant at terminal state remains unanswered.

Wiles and Bywater¹⁹⁰ examined the kinetics of methyl methacrylate initiated by *n*-butyllithium in toluene restricted their measurements to rather low monomer concentrations to avoid the problem of excessively high solution viscosity. The reaction is very rapid and that much of the butyllithium is consumed in the rapid formation of very low molecular weight polymer. A small fraction of the initiator is responsible for the high molecular weight material. The rate studies showed that the initial rapid growth is followed by a period of slower growth, which is internally of first order in monomer concentration. This is supported by the authors as the establishment of a steady state. This is supported by the observation that addition of more monomer to complete polymerization of the first batch caused a rate of polymerization close to that established in the later stage of the first batch. The authors found that the polymerization process is a simple scheme, and they were unable to offer a complete explanation.

Cottam, Wiles, and Bywater¹⁹¹ reported a study of polymers prepared by the *n*-butyllithium initiator in toluene at -30° C. It was found that the whole molecular weight distributions which can be attributed to a single mechanism, one of which occurs at low molecular weight region. This bimodal phenomenon was observed for conversions as well as for polymers representing various fractions of a whole polymer is not the whole. Weakley and coworkers¹⁹² also observed a similar bimodal distribution explained in terms of a combination of two mechanisms by simultaneously occurring mechanisms.

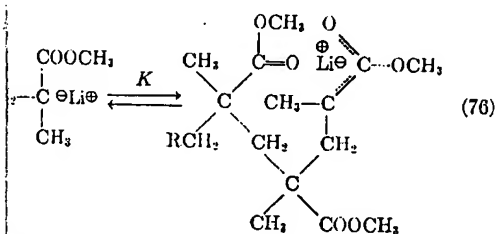
Wiles and Bywater¹⁹³ suggested that the wide differences in isotacticity of the polymer formed by different *n*-butyllithium ratios as well as the changes in rate of polymerization, may be accounted for in terms of the presence of a reaction mixture. It is possible that methoxy

based on the proposed reaction scheme requires drastic equations are valid only at very low conversions are not important.

Polymerization of methyl methacrylate in toluene in the range of -50° to -78° C with 9-fluorenyl-long ultraviolet absorption of the fluorenyl group was of initiator fragments bound to the polymer chain. Labelled acetic acid allows one to calculate the constants. Comparison of these two independent measurements which were active when the terminator was it was concluded that one fluorenyl group becomes polymer chain and essentially all of the initiator reacts ends after mixing, and termination reactions are very between 75% and 100% of the polymer chains were of polymerization.

Propagation, and the lack of termination should produce contrary to this prediction, fractionation¹⁸⁸ indicated distribution of these polymers is bimodal; (2) more chains has a molecular weight less than 2000; (3) chains add tritium upon reaction with tritium, therefore, result from permanent termination (4) distribution of the high polymer fraction from sufficiently broad to approximate log-normal distribution in toluene causes decreases in isotacticity and distribution. Kinetics were measured in 90% toluene/CH₂Cl₂ at -60° C. These experiments showed that: (1) reaction appears to be first order in monomer and remains constant; (2) plots of $-\ln M/M_0$ as a function of time (monomer concentrations at time t and 0, respectively) give a conversion intercept at zero time; (3) this conversion intercept form a species containing one fluorenyl group and plots of number-average molecular weight as a function of time give a conversion intercept at zero time, regardless of the ratio of monomer to that of initiator, and that intercept is the same as just mentioned (one fluorenyl group and three

mechanism which is based on all these data as follows: monomer addition proceeds until three monomer units are added; (4) percentage of the total number of chains started by forming the cyclic complex to which further addition is difficult.



reaction in the probability of cyclization when the

chain length reaches eight or nine monomer units. These chains can then grow to high molecular weights. It is necessary to postulate that a steady state in active centers is achieved to account for the first-order kinetic dependence of monomer up to high conversion. The authors originally suggested that the probability of cyclization is a function of the configurations of the last three monomer units in the chain, and that the decrease in probability of cyclization after the chains exceed eight to ten monomer units is due to the formation of helical conformations. The latter favors isotactic propagation. However, their later work¹⁸⁹ showed that the pseudo termination of the low molecular weight polymers takes place during both syndiotactic and isotactic propagations. The hypothesis that differences in the equilibrium constants for cyclization are the predominant results of difference in configurations of the last three units at the end of polymer chain was abandoned. The question of how initial conditions affect the equilibrium constants for cyclization to a pseudo terminal state remains unanswered.

Wiles and Bywater¹⁹⁰ examined the kinetics of the polymerization of methyl methacrylate initiated by *n*-butyllithium in toluene solution at -30° C. They restricted their measurements to rather low monomer/initiator ratios to avoid the problem of excessively high solution viscosity. They found that the initiation reaction is very rapid and that much of the butyllithium is accounted for in the initial rapid formation of very low molecular weight polymer. Once formed, this low molecular weight material did not add further monomer and so was not active. Only a small fraction of the initiator is responsible for the formation of high molecular weight material. The rate studies showed that the initial fast consumption of monomer is followed by a period of slower growth, which leads to a final fast reaction internally of first order in monomer concentration. This latter stage was considered by the authors as the establishment of a steady concentration of reactive centers. This is supported by the observation that addition of further monomer after the complete polymerization of the first batch caused a first-order monomer consumption close to that established in the later stage of polymerization. The number of active centers which lead to high polymer seems to depend in a complex manner upon initial butyllithium and monomer concentrations. It was also shown that the slow growth period is associated with a lower degree of isotacticity in the high polymer, whereas the faster reaction stage produces polymer of nearly 90% isotactic structure. The authors found that the polymerization process was much too complex to fit a simple scheme, and they were unable to offer a complete explanation.

Cottam, Wiles, and Bywater¹⁹¹ reported a study of the fractionation of a number of polymers prepared by the *n*-butyllithium initiation of methyl methacrylate in toluene at -30° C. It was found that the whole polymers have unusually wide molecular weight distributions which can be attributed to a combination of two narrower distributions, one of which occurs at low and another at a higher molecular weight region. This bimodal phenomenon was observed for polymers at lower conversions as well as for polymers representing complete conversion of monomers. Proton magnetic resonance measurements showed that the degree of isotacticity of various fractions of a whole polymer is not the same at all molecular weights. Weakley and coworkers¹⁹² also observed a similar bimodal distribution which was explained in terms of a combination of two much narrower distributions, produced by simultaneously occurring mechanisms.

Wiles and Bywater¹⁹³ suggested that the wide distributions of molecular weight, differences in isotacticity of the polymer formed with different methacrylate-butyllithium ratios as well as the changes in rate and degree of isotacticity during reaction, may be accounted for in terms of the presence of lithium methoxide in the polymerization mixture. It is possible that methoxide anions, which are incapable of

initiating polymerization by themselves, participate in the propagation step and affect the rate and stereochemistry of the reaction. Wiles and Bywater visualized the polymerization of methyl methacrylate with butyllithium in toluene as having two types of active centers. The first type is the straightforward ion-pair and the other involves methoxide. Lithium methoxide could be formed from the interaction of butyllithium and the ester group of the monomer, from the interaction of polymer-Li and the ester group of the monomer¹⁹⁴, and from active polymer chains by cyclization¹⁹⁵.

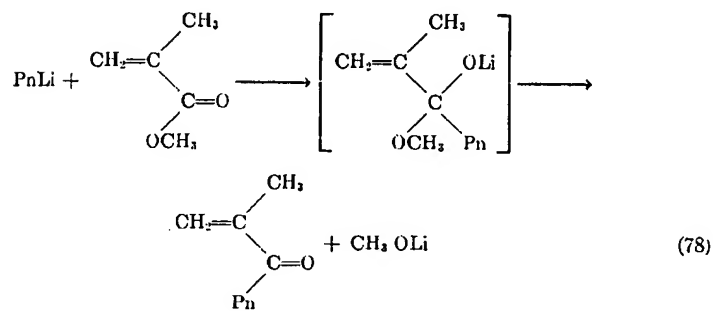
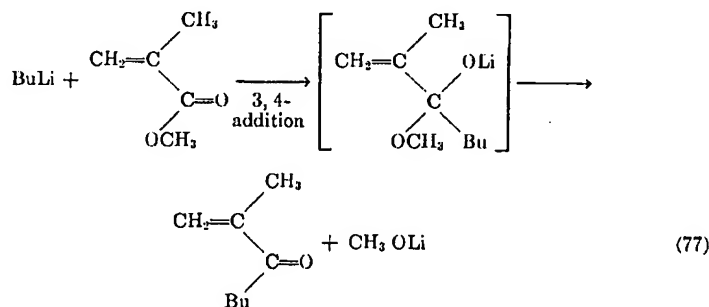


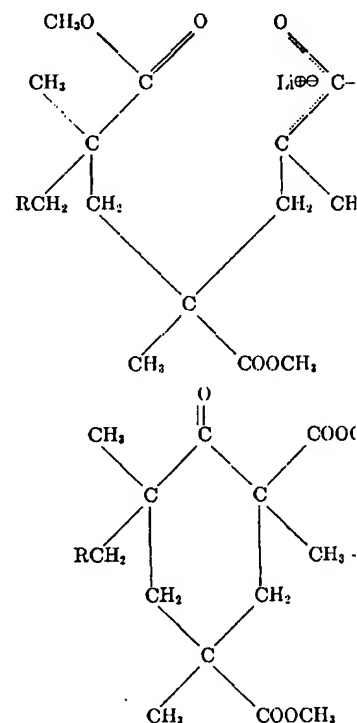
TABLE XII

FATE OF *n*-BuLi IN THE REACTION WITH METHYL METHACRYLATE IN HEXANE AT -70°C ¹⁹²

<i>n</i> -BuLi, mmole/liter	39.6	30.1	25.3	7.9	30.1
methyl methacrylate, mmole/liter	380	380	380	380	34.4
Product, %					
A	9	18	23	42	19
B	1	1	4	1	1
C	17	30	28	<1	30
D	1	1	4	<1	6
E	1	1	1	1	37
Polymer ^a	71	49	40	55	7

^a By difference.

ALKYLLITHIUM POLYMER

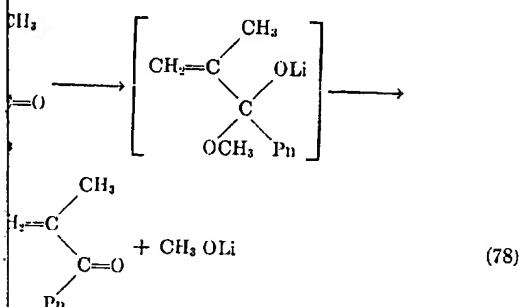


Cubbon and Margerison suggested¹⁹⁶ that part of Wiles and Bywater is perhaps caused by the product compete with methyl methacrylate for initiator to

With butyllithium it was shown¹⁹³ that most of first few seconds at -30° in toluene. The rapid for the attack of butyllithium on ester groups or to the (tion) step involved in the formation of low poly formed is greater than the number of molecules evidence, it was concluded that most of the initial attack on the ester group of the monomer. This is temperature and the nature of the solvent.

The polymerization of methyl methacrylate in *n*-hexyllithium was reported¹⁹⁷. Much simpler kinetic initiator than with butyllithium initiator. The amount is much smaller and is approximately a constant number of molecules of low molecular weight product order in both monomer and initiator concentration. growing polymer chains is linearly dependent upon.

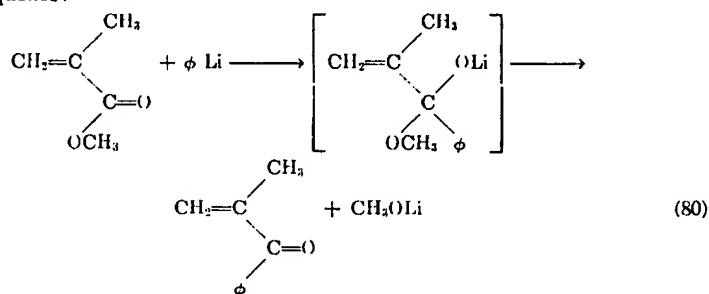
The polymerization of methyl methacrylate with butyllithium¹⁹⁸ and fluorenyllithium^{199,200} as is complicated by side reactions and termination regulated the reaction between equimolar quantities of lithium in diethyl ether at room temperature. The



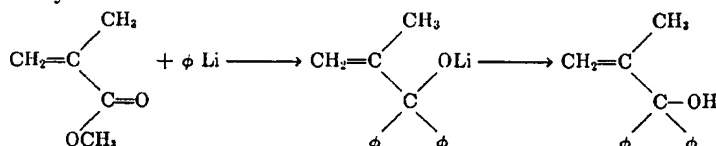
39.6	30.1	25.3	7.9	30.1
380	380	380	380	34.4
9	18	23	42	19
1	1	4	1	1
17	30	28	<1	30
1	1	4	<1	6
1	1	1	1	37
71	49	40	55	7

The polymerization of methyl methacrylate in tetrahydrofuran was studied with butyllithium¹⁹⁸ and fluorenyllithium^{199,200} as initiator. Polymerization again is complicated by side reactions and termination reactions. Schreiber²⁰¹ has investigated the reaction between equimolar quantities of methyl methacrylate and phenyllithium in diethyl ether at room temperature. The main product which was isolated

after hydrolysis was diphenylisopropenylcarbinol. This product must arise from the reaction sequence:



followed by



The above reactions are analogous to those proposed by Cubbon and Margerison for the butyllithium reaction in toluene.

Kawabata and Tsuruta²⁰² investigated the reaction made of *n*-butyllithium with methyl methacrylate in hexane and in tetrahydrofuran. Identification of products formed was made by comparing retention time and peak shape in vapor-phase chromatography with the authentic samples or compounds having a similar chemical structure. Their results are summarized in Tables XII and XIII.

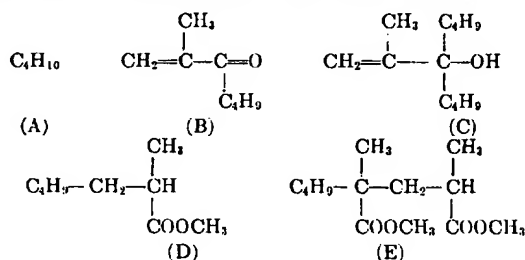


TABLE XIII

FATE OF *n*-BuLi IN THE REACTION WITH METHYL METHACRYLATE IN TETRAHYDROFURAN AT -70°C ²⁰³

<i>n</i> -BuLi, mmole/liter	63.0	40.1	40.1	40.1	37.8	12.6
Methyl methacrylate, mmole/liter	380	380	92.6	36.2	190	380
Product, %						
A	17	26	28	29	28	45
B	11	12	11	9	12	17
C	39	18	62	63	16	0
D	0	0	0	0	0	0
E	4	0	0	0	0	0
Polymer ^a	20	44	0	0	44	38

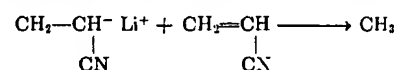
^a By difference.

These investigators also detected methanol in lithium and methyl methacrylate. But the amount found by Wiles and Bywater.

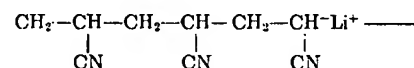
It is apparent that the polymerization of *n*-lithium initiator involves many side reactions and is complex for analysis at this time.

The polymerization of acrylonitrile with BuLi: Miller²⁰³ investigated this at -78°C and found only introduced produces high polymer. The initial resulting polyacrylonitriles have a broad molecular weight distribution.

Ottolenghi and Zilkha²⁰⁴ studied the polymerization of formamide with butyllithium in the temperature range of initiator concentrations investigated, butyllithium initiates growing chains. Two different termination reactions were found, depending upon the initiator concentration, termination is bimolecular by chain transfer.



while, at low concentrations, termination was a disproportionation reaction of the growing chain ends.



The existence of chain transfer only at high initiator concentrations and the possibility of butyllithium participation in the termination reaction.

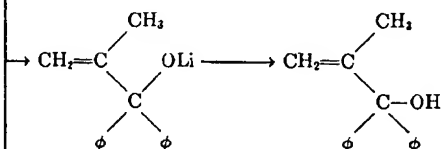
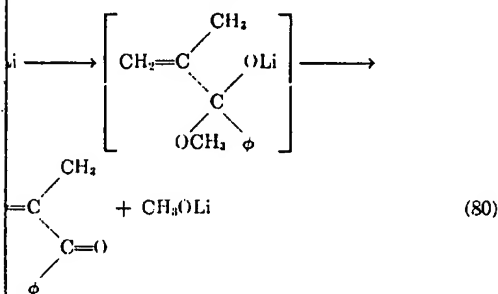
SUMMARY

The kinetics of alkyllithium initiated polymerization of methyl methacrylate in Rubber Reviews for 1970. It contains nine sections on organolithium compounds, rate of polymerization, initiation, molecular weight and molecular weight distribution, diene and vinyl monomers in polar solvents, copolymerization of polar monomers. A total of 205 references are cited.

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propenylcarbinol. This product must arise from the



as to those proposed by Cubbon and Margerison in toluene.

Investigated the reaction made of *n*-butyllithium with methyl methacrylate in tetrahydrofuran. Identification of products by retention time and peak shape in vapor-phase chromatography of samples or compounds having a similar chemical structure is summarized in Tables XII and XIII.

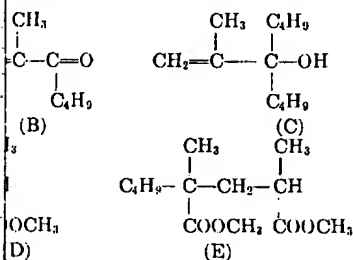


TABLE XIII

REACTION WITH METHYL METHACRYLATE IN TETRAHYDROFURAN AT -70°C^{202}

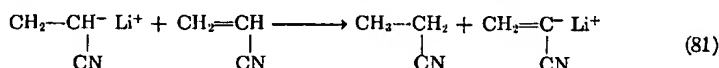
63.0 380	40.1 380	40.1 92.6	40.1 36.2	37.8 190	12.6 380
17	26	28	29	28	45
11	12	11	9	12	17
39	18	62	63	16	0
0	0	0	0	0	0
4	0	0	0	0	0
29	44	0	0	44	38

These investigators also detected methanol in the reaction mixture of *n*-butyllithium and methyl methacrylate. But the amount of methanol was less than that found by Wiles and Bywater.

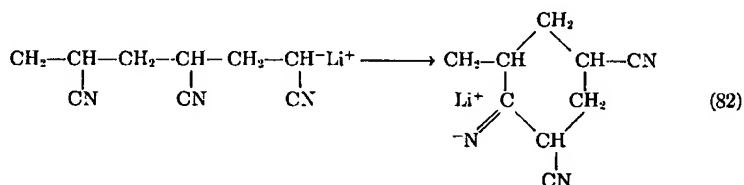
It is apparent that the polymerization of methyl methacrylate with alkyllithium initiator involves many side reactions and the kinetic behavior is too complex for analysis at this time.

The polymerization of acrylonitrile with BuLi in toluene is also very complex. Miller²⁰³ investigated this at -78°C and found only about 5% of the *n*-butyllithium introduced produces high polymer. The initial reaction is very rapid and the resulting polyacrylonitriles have a broad molecular weight distribution.

Ottolenghi and Zilkha²⁰⁴ studied the polymerization of acrylonitrile in dimethylformamide with butyllithium in the temperature range -50° to 0°C . Over the wide range of initiator concentrations investigated, only a small portion of the added butyllithium initiates growing chains. Two different termination reactions were found, depending upon the initiator concentration. At high butyllithium concentrations, termination is bimolecular by chain transfer to monomer,



while, at low concentrations, termination was monomolecular, by an inner cyclization reaction of the growing chain ends.



The existence of chain transfer only at high initiator concentration suggests the possibility of butyllithium participation in the transfer reaction.

SUMMARY

The kinetics of alkyllithium initiated polymerizations is reviewed for publication in Rubber Reviews for 1970. It contains nine sections: introduction, the structure of organolithium compounds, rate of polymerization, rate of propagation, rate of initiation, molecular weight and molecular weight distribution, polymerization of diene and vinyl monomers in polar solvents, copolymerizations, and polymerizations of polar monomers. A total of 205 references are cited.

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Styrolux⁺ and Styroflex⁺ - From Transparent High Impact Polystyrene to New Thermoplastic Elastomers

Syntheses, Applications and Blends with other Styrene based Polymers

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SUMMARY: Styrolux and Styroflex are styrene and butadiene based block copolymers prepared by butyllithium initiated anionic polymerization. Styrolux is a transparent, tough and stiff thermoplastic material for high speed processing. Its specially designed molecular structure allows homogeneous mixing with general purpose polystyrene maintaining the transparency. Styroflex is a newly commercialized product with the mechanical behavior of a thermoplastic elastomer, e.g. low modulus and yield strength, high elongation and excellent recovery. High transparency and thermal stability give the competitive edge over conventional styrene-butadiene elastomers. Styroflex, Styrolux and general purpose polystyrene form a unit construction system e.g. for transparent film materials and injection molded parts with fine-tunable hardness and toughness.

Introduction

Basic properties of noncrystalline polymers are determined by the value of the glass transition temperature T_g in respect to ambient temperature. Polymers with low T_g are referred to as rubbers and behave as viscoelastic liquids. Typical properties comprise elastic recovery, large elongation at break, and softness. To avoid tack and cold flow chemical crosslinking (vulcanization) is required for many applications. On the other hand high T_g resins are stiff and hard, but commonly break when elongated beyond a few %. Well defined block copolymers with at least one block sequence hard-soft-hard offer the chance to combine the advantages of both groups of commonly incompatible materials while maintaining transparency (Fig. 1).

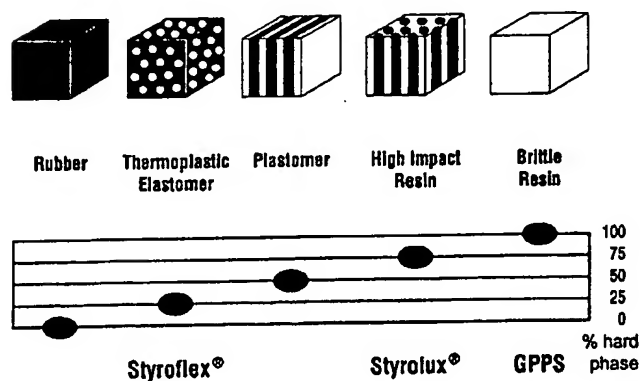


Fig. 1. Mechanical property range of block copolymers. Note: Styroflex contains ~70% soft phase, but only ~35% butadiene.

* Styrolux and Styroflex are registered trademarks of BASF Aktiengesellschaft

The matrix phase basically determines the bulk properties like mechanical behavior and polarity. Thus thermoplastic elastomers exhibit predominantly elastic deformation. They are characterized by a rubber matrix containing inclusions of the hard spheres or cylinders consisting of high T_g end blocks as molecular anchors. The ratio of plastic to elastic deformation increases with the content of the hard phase. Fairly soft "plastomers" with a 50/50 hard-soft ratio and cocontinuous morphology do not have substantial elastic recovery and no pronounced yield point, but show extended plastic deformation due to shear yielding¹⁾. Reduction of the rubber content to 25% in simple symmetrical triblock copolymers leads to high modulus but brittle thermoplastic materials. The challenge has been to develop stiff resins with a low rubber content while preserving the ability of plastic deformation¹⁾ and in consequence impact strength.

Styrolux

Styrolux, the transparent and tough polystyrene of BASF with styrene butadiene block structure, is used in applications like packaging film, beakers and injection molded parts. This type of polymer was introduced in the late fifties²⁾ and has subsequently been improved. It is now a steadily growing specialty in a.m. applications. Roughly 80% of Styrolux is blended with general purpose polystyrene (GPPS)³⁾.

In order to understand the role of transparent and tough polystyrene like Styrolux as blend component, its molecular design is briefly discussed. All Styrolux grades except the later described KR 2691, a linear, symmetrical S-B-S triblock, consist of unsymmetrical star block copolymers. When Styrolux without further specification is mentioned later in the text the term always refers to star polymer grades. The Styrolux grades cover a butadiene content from about 20 to 30%, differing in their toughness/stiffness ratio. Styrolux combines a substantial yield point (25-35 MPa) with plastic deformation up to 300%.

Synthesis, Structure and Morphology of Styrolux. Transparent and tough polystyrene is prepared by sequential anionic polymerization, where butyllithium may be added in more than one charge. A possible synthesis consists of the formation of a long styrene block in the first step, followed by further addition of butyllithium and styrene, thus yielding short styrene blocks. The molar ratio of short to long chains is significantly larger than 1. In Styrolux, a mixture of styrene and butadiene is finally added, resulting in a butadiene/styrene block with a tapered block transition. This mixture consisting of short, butadiene-rich and long, styrene-

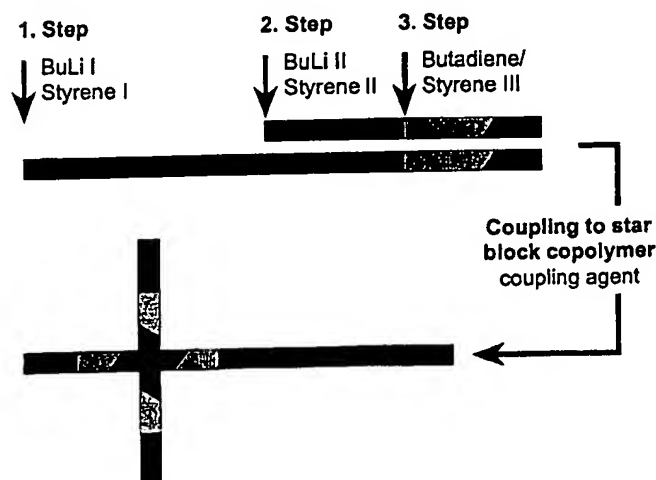


Fig. 2. Synthesis of Styrolux.

rich triblocks is coupled with an oligofunctional coupling agent giving on average an unsymmetrical star polymer with about 4 arms (Fig. 2)⁴⁾. The coupling reaction is of course a statistical process and all possible combinations of long and short arms are observed in an amount predicted by Pascal's triangle, taking the molar ratio into consideration.

The morphology of Styrolux does not fit into the common morphology scheme of styrene/butadiene block copolymers with spheres, cylinders and lamellae as basic morphologies. Fig. 3 left and center shows TEM micrographs of a compression-molded Styrolux sample. At first glance, the impression is one of an irregular, wormlike morphology. Styrene and butadiene form an interpenetrating network with styrene as the predominant phase (Fig. 3 left). A closer look reveals that the butadiene "lamellae" are often split and appear to contain small styrene cylinders and spheres. The difference in scale is remarkable (diameter): large styrene "worms": 25 nm, small styrene inclusions in butadiene: 6 nm, butadiene "lamellae": 8 nm. One explanation might be that long and short styrene blocks partly demix. In particular the short styrene block in the core of the star polymer might form a separate phase. [This notion is also supported by DSC measurements discussed later. The glass transition temperature of the hard phase is unusually broad and stretches from 105 down to 30°C suggesting at least an inhomogeneous polystyrene phase.]

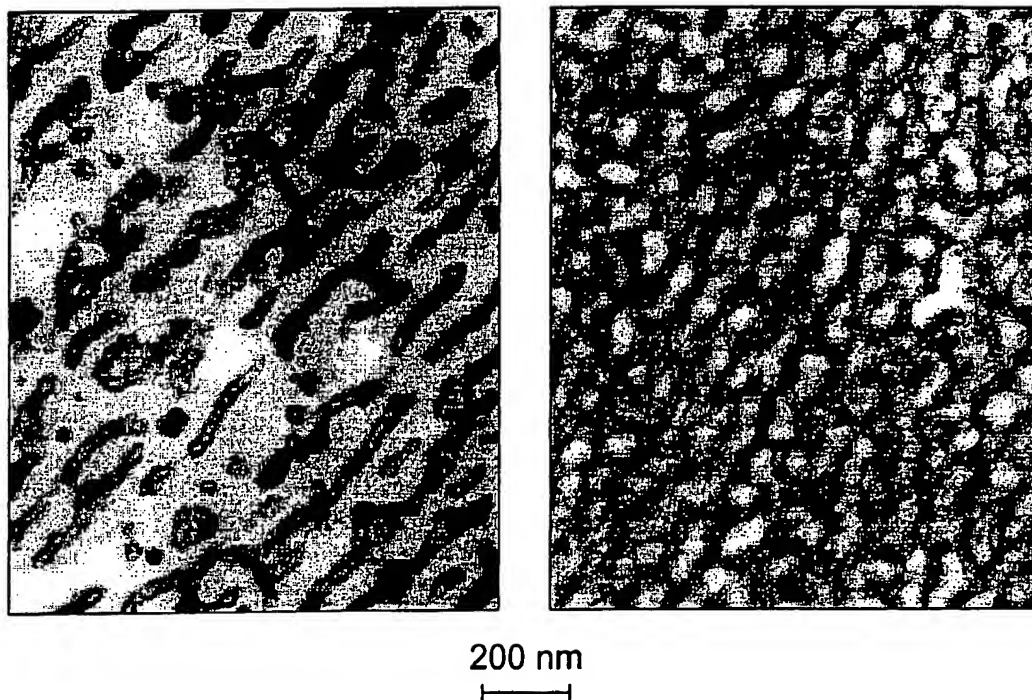


Fig. 3. TEM micrographs of Styrolux/GPPS blend (40/60) (left) and neat Styrolux (right).

Styrolux/GPPS Blends. In blends with polystyrene the "double lamellae" continue to exist unchanged. Only the large styrene domains are widened (Fig. 3 right). Apparently the long styrene blocks of Styrolux are directed towards the GPPS containing domains.

Transparency runs through a minimum for 30/70 Styrolux/GPPS blends (Fig. 4), but for film applications the drop is negligible. GPPS is added both on grounds of economy and to modify specific properties. Stiffness (modulus of elasticity), hardness and heat distortion resistance (Vicat B) increase when GPPS is added, whereas the toughness decreases.

Structure and Synthesis. To meet these goals we chose a symmetrical hard-soft-hard structure typical for TPEs with a block length ratio of about 15:70:15⁵⁾. The hard segments consist of polystyrene, but instead of a butadiene soft segment we introduced a statistical SB sequence with a glass transition temperature of approx. -30°C and an S/B ratio of approximately 1. Thus the overall styrene content of Styroflex reaches almost 70% which is in a range known for transparent, impact modified polystyrene like Styrolux. The benefit of this structural variation is a drastically increased molecular weight (140,000 vs. 70,000 g/mol) while retaining the same viscosity or melt flow rate⁶⁻⁸⁾. Furthermore, a low 1,2-vinyl content is required for superior thermal stability due to reduced crosslinking.

The polymer is prepared by butyllithium-initiated sequential anionic polymerization in cyclohexane (Fig. 5). In order to generate the statistical SB block the presence of a randomizer is required⁹⁾. Commonly at least 0.2 to 0.5 vol% of tetrahydrofuran (THF) are added, based on cyclohexane. Using less THF renders a styrene end block which changes the hard-soft-ratio and results in the loss of elastic recovery. Unfortunately THF changes the butadiene microstructure by raising the 1,2-vinyl content from about 8 % in pure cyclohexane up to 30% in the presence of 0.25 vol% THF. Since 1,2-vinyl units undergo crosslinking more readily than 1,4 units, the thermal stability of the SB rubber is reduced. In this respect the THF content has to be kept as low as possible, accepting some gradient from butadiene to styrene. Dividing the SB block into several short blocks, supports however the formation of a homogeneous soft phase. As an alternative, potassium alkoxides can be added as randomizers. Most favorable are sterically hindered tertiary alkoxides like triethyl carboxide¹⁰⁾. Best results are obtained with a K/Li molar ratio of 1:30^{10,11)}. The even incorporation of styrene and butadiene could be shown by taking samples during the copolymerization and analyzing the butadiene content.

There are three basic synthesis routes to Styroflex (Fig. 5): sequential polymerization, coupling of a living S-SB diblock, or bifunctional initiation¹²⁾. Bifunctional coupling agents X such as dichlorodimethylsilane and butanediol diglycidyl ether give almost quantitative coupling yields. Carboxylic esters like ethyl acetate work only well when donor solvents are absent. In the presence of THF the coupling yield drops to 30-40%.

Essentially ether-free bifunctional initiators for highly bifunctional growing polymers have been developed by BASF¹³⁾. At the time our goal was to find a starting system for the preparation of 1,4-polybutadienediol. Starting materials for the bifunctional initiators are alkylated, particularly methylated, 1,1-diphenylethenes, and β -alkylstyrenes. Reductive coupling with lithium metal in an ethylbenzene/ethyl ether mixture yields the desired 1,4-dilithiobutane derivatives in quantitative yield. The ether serves as charge transfer catalyst. In the case of 1,1-diphenylethylene derivatives at least two methyl groups are required to achieve solubility in ethylbenzene. Best suited in terms of accessibility and side reactions is 1-(3,4-dimethylphenyl)-1-phenylethene, which can readily be made by addition of ortho-xylene to styrene in the presence of sulfuric acid followed by dehydrogenation. After the reductive coupling the ether and ethylbenzene are stripped under reduced pressure leaving the dilithiobutane as a deep red, viscous liquid, which tends to crystallize after several hours. Hydrolysis and GC analysis did not show any residual ether. At least one equivalent THF per dilithiobutane remains ligated however, if THF instead of ether is used. The dilithiobutane derivatives themselves proved to be poor bifunctional initiators. About 60% monofunctional growth has been observed. A possible explanation is fast lithium hydride elimination during the initiation step. In order to obtain a useful bifunctional initiator the dilithiobutane is reacted at 0°C with 10 equivalents of butadiene which plays the role of both activator and solvent. The resulting pale yellow oligomeric initiator, which is obtained as a viscous liquid, can be

diluted with cyclohexane, and virtually quantitative bifunctional initiation of butadiene and/or styrene is observed.

Morphology. Fig. 6 shows the TEM micrograph of a compression-molded Styroflex sample. Due to the phase/volume ratio of about 30% polystyrene in the block polymer, the transmission electron micrograph of Styroflex depicts spherical morphology with the SB rubber as matrix and polystyrene as spheres. The fuzzy borders of the spheres indicate an extended interphase typical of a system close to the order-disorder transition (ODT). The repulsive interaction between the polystyrene and the SB phase is greatly diminished compared to a polystyrene/polybutadiene system. Styroflex has a higher molecular weight than commercial SBS TPEs however, which in turn favors phase separation. When cooling from the melt within a few minutes no long range order develops, but the arrangement of the styrene domains is quite regular yet. Styrene domains are surrounded predominantly hexagonally by their neighbors. The domain identity period is about 39 nm.

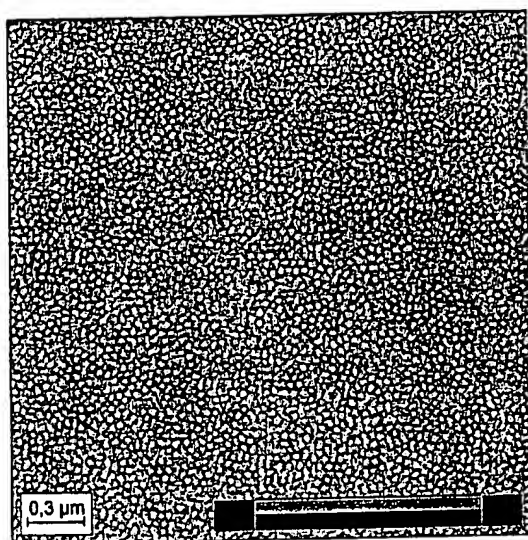


Fig. 6. Transmission electron micrograph of Styroflex.

Thermal Properties. The DSC analysis (Fig. 7) shows the glass transition temperature of the soft phase at around -17°C . The long flat slope up to 80°C indicates an extended interphase ending in a barely separated hard phase. We proved that this is not an

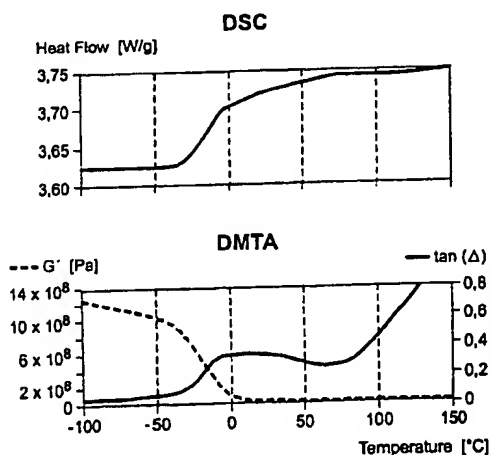


Fig. 7. Top: DSC analysis of Styroflex. Sample quenched from melt; heating rate 20 K/min. Bottom: Dynamic mechanical thermoanalysis (DMTA) of Styroflex.

effect of the heterogeneity of the SB rubber phase by synthesizing and analyzing the pure rubber block. In this case the glass transition was limited to a temperature range between -30 and 0°C.

DMTA measurements (Fig. 7) on Styroflex show two softening points around -20°C and +70°C, which are in good agreement with the DSC measurement.

Rheology. Fig. 8 depicts the relationship between the melt viscosities at 190°C and the shear rate for three different triblock copolymers. Styroflex is compared with Styrolux KR 2691 (BASF), which is a symmetrical SBS triblock with a molecular weight (MW) of approx. 70 000 g/mol and a butadiene content of about 26%, and with Kraton D 1102 (Shell), an SBS-type thermoplastic elastomer with a MW of approx. 70 000 g/mol and a butadiene content of about 70%. It can be seen that the three triblock copolymers behave quite differently. At low shear rates the melt viscosities of both Styroflex and Kraton D show little rate dependence in contrast to Styrolux KR 2691, where a decreasing rate is accompanied by a pronounced increase in viscosity, which is characteristic of thixotropic behavior. At high shear rates both Styrolux KR 2691 and Styroflex show significantly more shear thinning compared to Kraton D 1102, indicating good processability. Rheological measurements have been performed between 110 and 220°C in order to determine the ODT, which is found at 145°C. This temperature is well below the favored Styroflex processing temperature (170 - 210°C). Thus, the production of thin films with diminished residual melt history is facilitated. The low ODT is a key advantage over conventional SBS block copolymers.

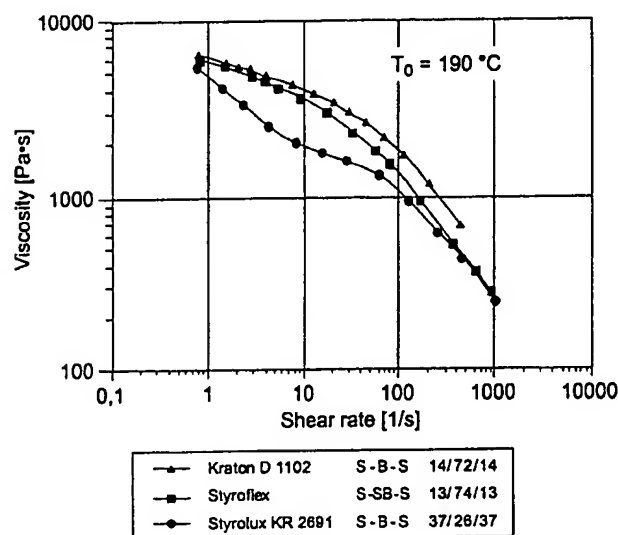


Fig. 8. Rheological behavior of different symmetrical triblock copolymers at 190°C.

Mechanical Properties. The mechanical behavior of Styroflex is that of a typical thermoplastic elastomer (Fig. 9). It appears to be somewhat harder than a classical SBS TPE. With an annealed specimen, an ultimate elongation at break of approx. 900% can be achieved, whereas typical SBS polymers fail at elongations of about 1000%. Similar behavior is observed with metallocene polyethylene.

At elongations well below failure, Styroflex follows Hooke's law. In contrast Styrolux KR 2691, a highly transparent and stiff polystyrene with symmetrical SBS triblock structure and a butadiene content comparable to that of Styroflex, has a pronounced yield point followed by plastic deformation. The tensile strength of PVC depends on the annealing time -

indicated by the dashed line. Styroflex films achieve a similar hardness to plasticized PVC due to molecular orientation.

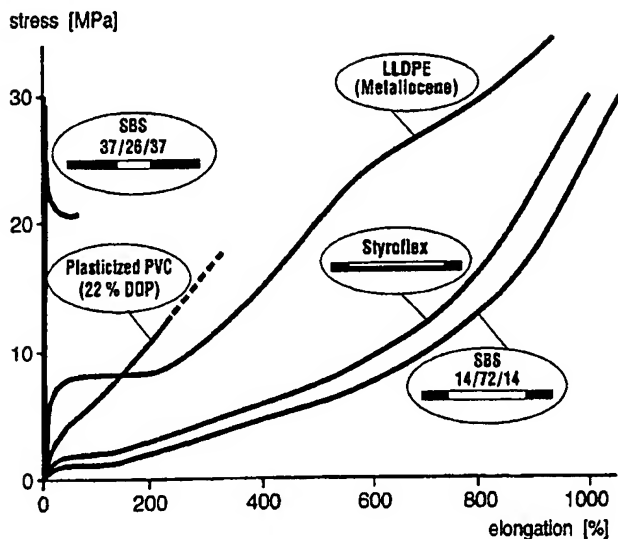


Fig. 9. Stress-strain diagram of compression-molded flexible materials.

Films designed particularly for food wrapping should maintain their smooth, optically attractive surface over an extended period of time even after touching, stapling and other manipulations, which might cause indentations. Therefore a virtually complete recovery of the stretched film is desirable.

Adapted hysteresis experiments have been performed in order to compare the recovery of Styroflex with other film materials (Fig. 10). The sample is elongated to 200% and released to zero stress at a constant rate of 100% per min. The additional recovery is then monitored for five minutes. The experiment is repeated up to 300 and finally 400%. The measurements prove that the recovery of Styroflex is in the range typical of SBS-TPEs and far better than plasticized PVC. In fact after 30 min. the residual deformation is reduced to only 3%.

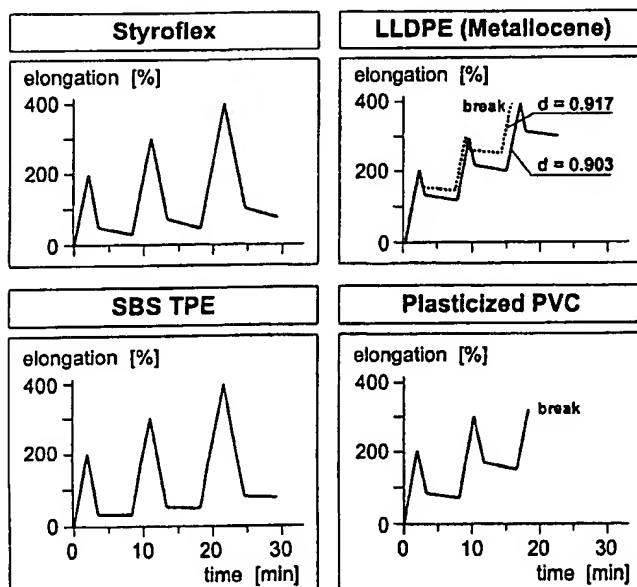


Fig. 10. Hysteresis of film materials.

comparison even the least crystalline metallocene linear low-density polyethylene (density 0.903) does not show a good recovery. The ratio of plastic to elastic deformation increases rapidly with density. Conventional SBS TPEs behave comparable to Styroflex, however their major drawbacks are poor thermoplastic processability and extensive thermal crosslinking. Thus, they are not applicable for sophisticated extruded and molded parts.

One of the predominant features of Styroflex is its high toughness. We compared Styroflex with plasticized PVC, metallocene PE and SBS elastomer (Tab. 1). The dart drop test proves its superior performance over plasticized PVC (note: oriented, extruded blown film was used for mechanical tests, see Tab. 1). Due to the orientation the Shore D hardness is roughly the same as that of PVC.

Tab. 1. Properties of Styroflex vs. plasticized PVC(20 w/w dioctyl adipate), metallocene PE and SBS elastomer (molded specimens)

	Test Conditions	Styroflex	Plast. PVC 20 % DOA	Metallocene PE	SBS elastomer
MVR (200°C/5kg) [ml/10']	ISO 1133	10-15	-	5	8
Dart drop [g] ^a	-	600	290	500	no film
Shore D hardness ^b	DIN 53505	39	36	42	20
Vicat A ^b [°C]	ISO 306	40	n.d. ^c	87	n.d. ^c
Elongation at break (%)	ISO 527	>500	approx. 300	>500	>500
Transparency [%]	-	80	85	85	20
Elastic recovery	-	++	++	+/-	++
Time until crosslinking ^d , 250°C, [min]	-	19	decompos. at T > 220°C	>60	4

^aWeight (g) of a falling dart until failure of film sample. Film gauge $14 \pm 5 \mu\text{m}$

^bDetermined on compression-molded specimen ($T = 200^\circ\text{C} / 5 \text{ min}$). ^cn.d. = not detectable.

^dPressure increase of 5 bar in rheography experiment (explanation in text; see also Fig. 14).

Fig. 11 shows the improvements in thermal stability. A thermoplastic material at $T = 250^\circ\text{C}$ is extruded through a hole at constant rate. Pressure p increases with time due to crosslinking reactions in the melt. An (arbitrary) measure for "crosslinking" is the time after $\Delta p = 5 \text{ bar}$.

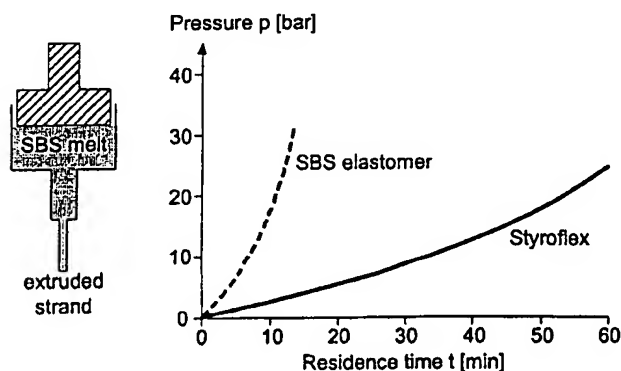


Fig. 11. Stability of SBS materials in melt. The time dependence of the extrusion pressure is a measure for the crosslinking rate.

Blends containing Styroflex

Styroflex/Styrolux Blend System. Extruder blends of Styroflex and Styrolux have been prepared for a number of mixture ratios. The transparency was virtually unimpaired by the blend composition and remained at the high level of the pure materials (Fig. 12), indicating homogeneity of the blends well below the wavelength of visible light. The mechanical properties such as modulus and elongation at break vary almost linearly with composition. This enables fine-tuning of hardness, toughness and flexibility of films and injection-molded parts.

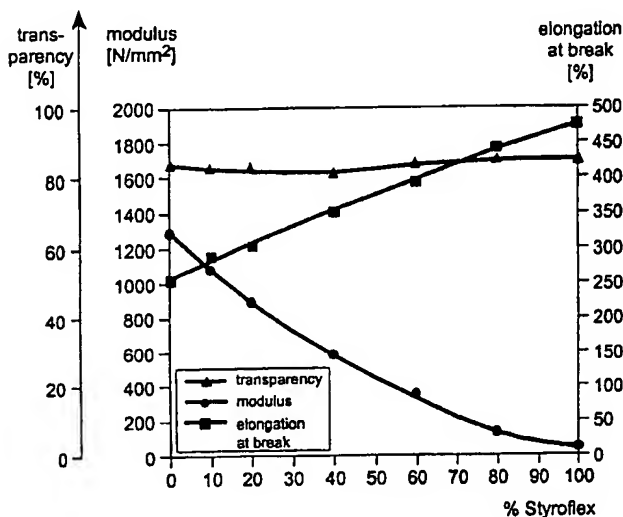


Fig. 12. Styroflex/Styrolux blend system: mechanical and optical properties.

In Fig. 13 the morphologies of pure Styrolux and Styroflex (top and bottom TEM) are compared with two blends. Styrolux (bottom) exhibits the already discussed complex wormlike morphology containing two different types of styrene domains with the long PS arms concentrated in the thick "lamellae". In Styrolux/Styroflex blends two phases become apparent. One phase is butadiene-rich and contains spherical PS domains, the other phase large styrene worms. The phase ratio does not reflect the mixture ratio of Styroflex and Styrolux, but the "Styroflex phase" seems to have a far larger volume ratio. The domain identity period is at roughly 15 nm less than half that of Styroflex. In view of the fact that the small styrene cylinders embedded in the butadiene lamellae disappear with increasing Styroflex content it appears most likely that Styroflex extracts the butadiene-rich stars containing only short arms and forms a new phase. Since this separation process occurs on a scale of about 80 nm transparency does not decrease.

The DSC analysis supports the conclusions from the TEM interpretations (Fig. 14). Only one soft phase is visible in both blends containing 20 and 60% Styroflex respectively, with average glass transition temperatures.

Styroflex / Styrolux

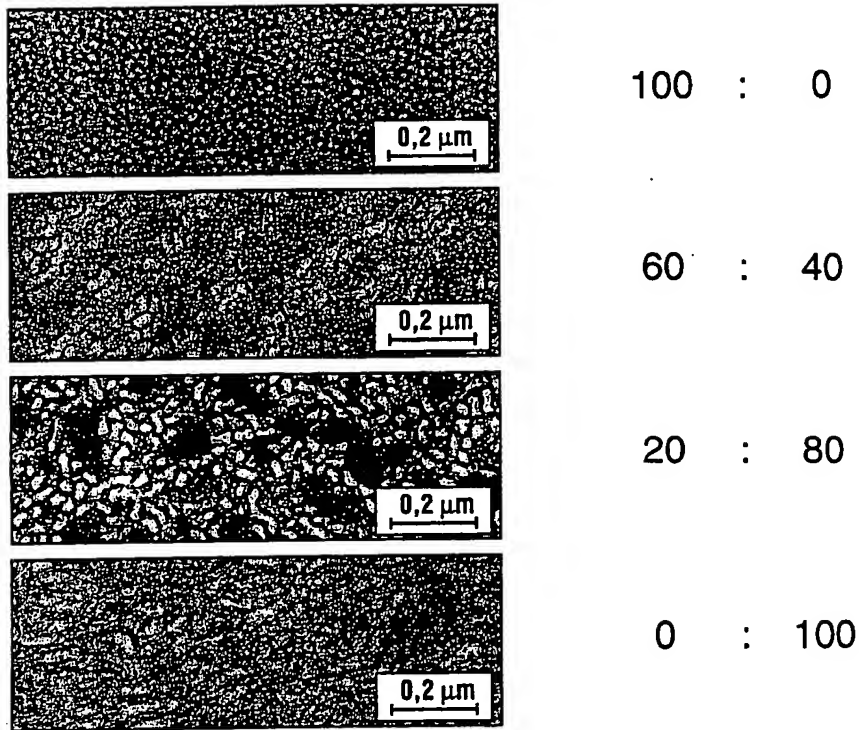


Fig . 13. Morphology of Styroflex/Styrolux blends.

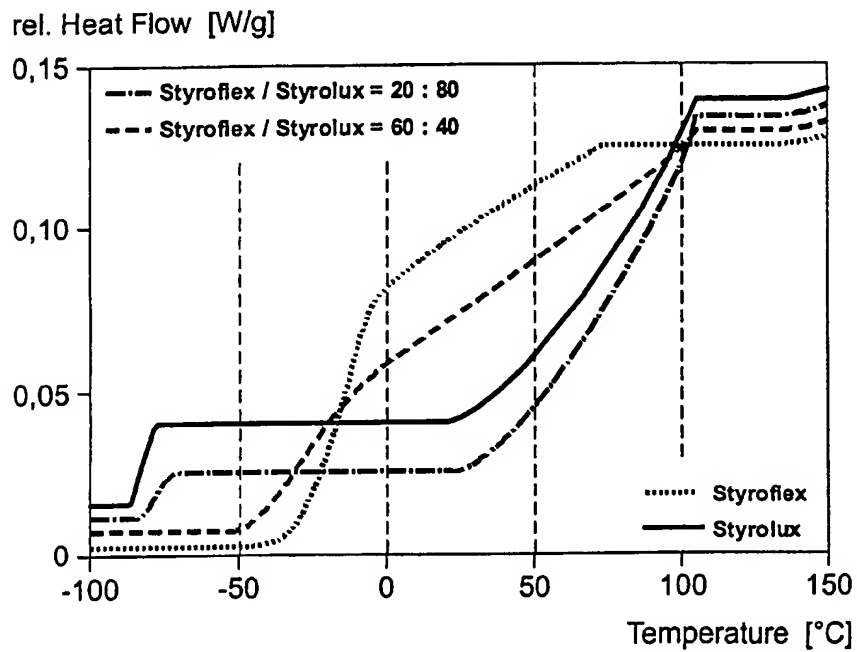


Fig . 14. Styroflex/Styrolux blend system: DSC analysis.

Styrolux/Styrolux/Polystyrene Blend System.

Adding Styroflex as a third blend component to the established Styrolux/GPPS system opens up new possibilities. The already discussed Styroflex/Styrolux blend system enables the property range between transparent polystyrene and soft thermoplastic elastomers to be covered which has recently been named "plastomer" by metallocene LLDPE producers due to the characteristic large plastic deformation. The stress-strain diagrams for a series of blends is depicted in Fig. 15 center, showing how the balance of elastic to plastic deformation shifts with increasing Styrolux content. The bottom diagram elucidates the transition from a tough, relatively soft to a stiff, but fairly brittle thermoplast. Mixing Styroflex with small amounts of general purpose polystyrene (GPPS) increases the hardness but retains the elasticity (Fig. 15 top). We also investigated the ternary blend system and found it to be a predictable and calculable unit construction system e.g. for tailor-made film materials. Styrolux mainly plays the role of a compatibilizer between Styroflex and GPPS. The fact that a certain degree of toughness can be achieved with a higher GPPS content than with binary Styrolux/GPPS blends makes the ternary system particularly attractive in respect to thermal stability and cost reduction.

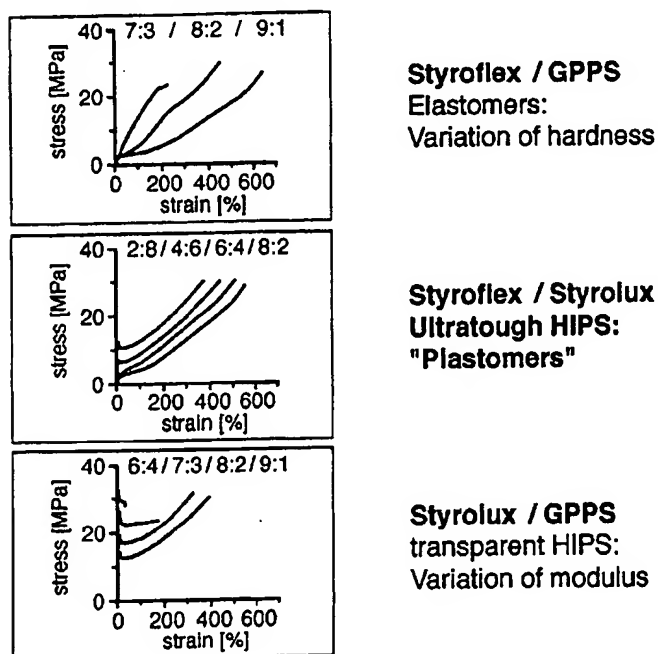


Fig. 15. Styroflex / Styrolux / GPPS blend system: stress-strain diagrams.

Conclusion

Styrolux and Styroflex are obtained by sequential anionic polymerization of styrene and butadiene. Styrolux is a stiff and tough resin, which retains its transparency when blended with general purpose polystyrene. Although containing only 25% butadiene it shows extended ductility explained by shear yielding processes. The highly unsymmetrical star block structure and the resulting complex morphology is thought to contribute to the favorable mechanical behavior.

Styroflex, the new BASF experimental styrenic polymer, combines the advantages of SBS elastomers (high toughness, recovery) with the properties of transparent, impact-modified SBS polymers like Styrolux (good processability, thermal stability, high transparency).

Together with Styrolux and general purpose polystyrene it forms a unit construction system e.g. for transparent film materials and injection molded parts allowing fine-tuning of hardness and toughness, representing the complete range of BASF's styrene/butadiene block copolymers (Fig. 1).

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